SYNTHESES, THERMOREORGANIZATIONS, AND SECONDARY DEUTERIUM ISOTOPE EFFECTS OF METHYLENE-3-VINYLCYCLOBUTANES

By

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Abstract of Dissertation Presented to the Graduate Council of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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The thermoreorganizations of methylene-3-vinylcyclobutane to 4-methylenecyclohexene and 1,1-divinyl-3-methylenecyclobutane to 4-methylene-2-vinylcyclohexene were investigated. Two mechanistic options were available for these rearrangements; one which involved the intervention of diradical intermediates, the other involved a concerted [3,3]-sigmatropic or Cope rearrangement.

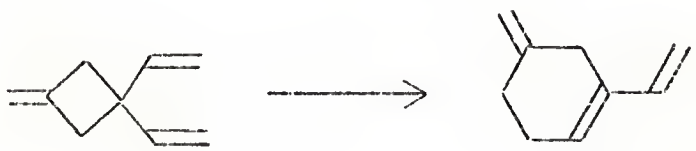
Activation parameters were determined for both of these pyrolyses. The heats of formation of their transition states were approximated by the group equivalent method, and these were consistent with the lower heats of formation, calculated for the speculated diradical intermediates. The low entropies of activation for these rearrangements could very reasonably be accounted for by the loss of internal

rotations of the vinyl group(s), and the subsequent restriction of a number of atoms to two rigid planar conjugated radicals.

The indication from the kinetic data that diradical intermediates intervene in these thermoreorganizations was corroborated by an intermolecular secondary deuterium isotope effect study where the rates of reaction of 1,1-divinyl-3-methylenecyclobutane were compared with 1,1-di(vinyl-$\underline{2}$,$\underline{2}$-$\underline{d}_2$)-3-methylenecyclobutane. The preponderant weight of analogy indicates that transformation of an isotopically substituted carbon from a trigonal to a tetrahedral orientation in the product should be associated with an inverse secondary deuterium isotope effect. However, a normal intermolecular isotope effect (k_H/k_D = 1.05±0.03) was observed at 99.9° which can be accounted for by a diradical process. From examination in the nmr of the product ratio, resulting from the thermolysis of 3-methylene-1-vinyl-1-(vinyl-$\underline{2}$,$\underline{2}$-$\underline{d}_2$)-cyclobutane, an intramolecular isotope effect (k_H/k_D = 1.14±0.07) was determined. The discrimination process which gives rise to this kind of secondary deuterium isotope effect is thought to involve a twisting motion of an isotopically substituted, terminal methylene group, resulting in a nonplanar pentadienyl radical with concomitant destruction of π-bonding at its terminus.

INTRODUCTION

The secondary deuterium isotope effect study for the thermal reorganization of 1,1-divinylcyclopropane (1) by Dolbier and Alonso[1] prompted an examination of the homologous and novel 1,1-divinyl-3-methylenecyclobutane (2).



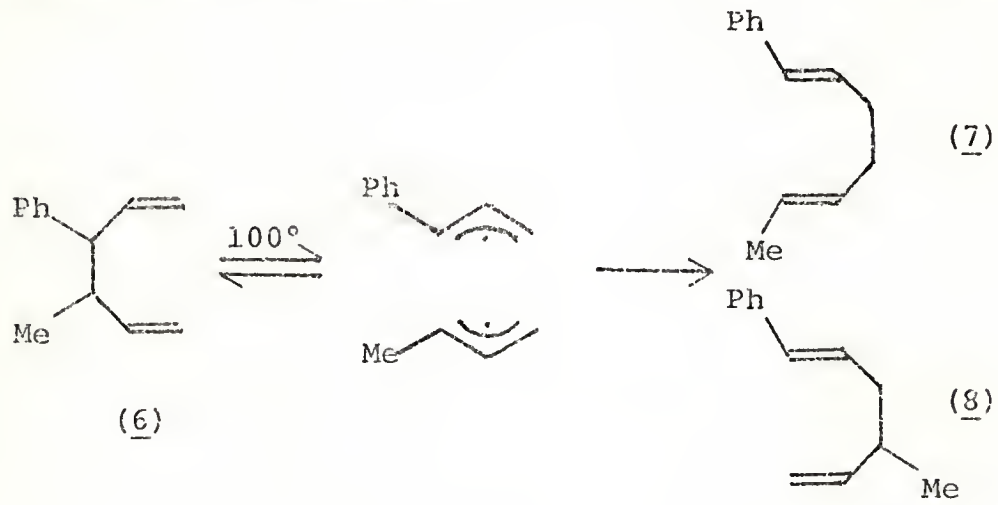
(2) (3)

The intriguing aspect of the latter, relative to (1), was that a mechanistic alternative was available for its thermal conversion to (3), that is, the potential existed that (2) might thermally convert to (3) by either diradical (4) or by a concerted [3,3]-sigmatropic rearrangement depicted by (5).

(4) (5)

The [3,3]-sigmatropic rearrangement was first discovered by Cope and coworkers.[2] In a study of substituted 1,5-hexadienes of which (6) was typical, they observed that (6) was not cleaved into a pair of allyl radicals upon

heating to 100°. Dissociation into two allyl radicals which could recombine in a second step to give cross products, as (8), was excluded, since only product (7) was formed. This process demonstrated a lack of response to

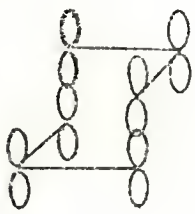


(6) (7) (8)

catalysts, changes in solvent medium and reaction phase.[3] Moreover, an additionally significant argument against cleavage of an acyclic 1,5-hexadiene to a bisallyl system in the rate-determining step was provided by the characteristically large negative values for entropies of activation (approximately -12 eu) measured for several Cope reactions.[4] The Cope rearrangement would thus pass through a cyclic multicentered transition state in which simultaneously (or nearly so) old bonds are broken while new bonds are formed.

One interesting feature of the Cope rearrangement is that the transition state could have either the four-centered chair (9) or the six-centered boat (10) conformation.[5] A classic experiment devised by von Doering

and Roth[6] was particularly successful in establishing which conformation was the preferred transition state. It involved the thermal rearrangement of meso-3,4-dimethyl-1,5-hexadiene (11) which at 225° almost exclusively yielded cis,trans-2,6-octadiene. This could only involve a four-centered chair-like transition state (9). If a six-centered boat-like conformation (10) were involved, only



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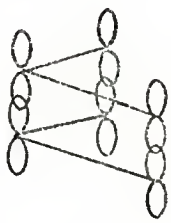

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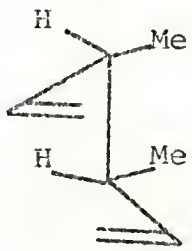
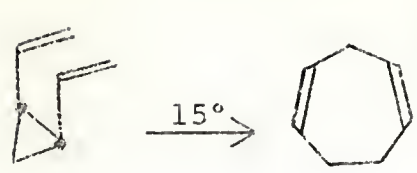
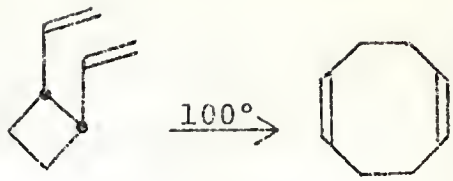


(11)

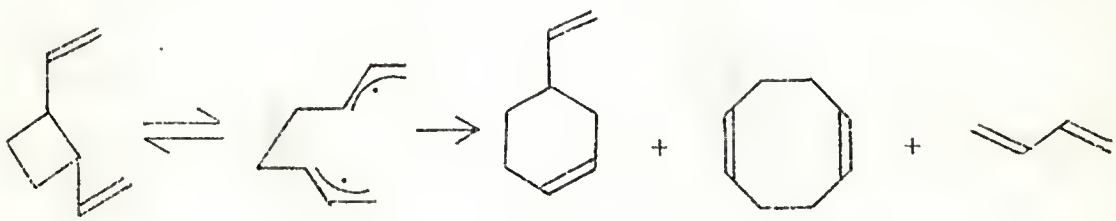
cis,cis- and trans,trans-2,6-octadiene would have resulted. They estimated that the difference in free energy in (11) between the four-centered (9) and the six-centered (10) conformation amounted to at least 5.7 kcal/mol. This corresponded nicely to MINDO/2 calculations which correctly predicted the chair-like transition state to be more stable than the boat by 6.6 kcal/mol.[7] Alternative theoretical treatments for the observed preference of the four-centered chair-like conformation in the concerted [3,3]-migrations of acyclic 1,5-hexadienes have been discussed.[8] However, in cis-1,2-divinylcycloalkanes, as (12)[9] and (14),[10] the boat-like transition state was energetically more accessible, and the thermal Cope reaction proceeded quantitatively.





(12) (13) (14) (15)

When neither a chair-like nor a boat-like conformation could be attained in the transition state, because the requisite geometry for a concerted [3,3]-sigmatropic migration would be energetically inaccessible, the chemical system would of necessity seek a lower energy diradical pathway if available. This would be specifically true for a small carbocyclic ring substituted with vinyl groups, where any incipient radical formed would be allylic and resonance-stabilized. A case in point is the trans-1,2-divinylcyclobutane (16) whose thermal rearrangement at 154° provided three products.[10] The major product 4-vinyl-cyclohexene (18) could arise either by diradical (17) or by a concerted [1,3]-sigmatropic migration. The latter was not supported by kinetic data nor analogy.[11, 12] The secondary product 1,5-cyclooctadiene (15) could also arise

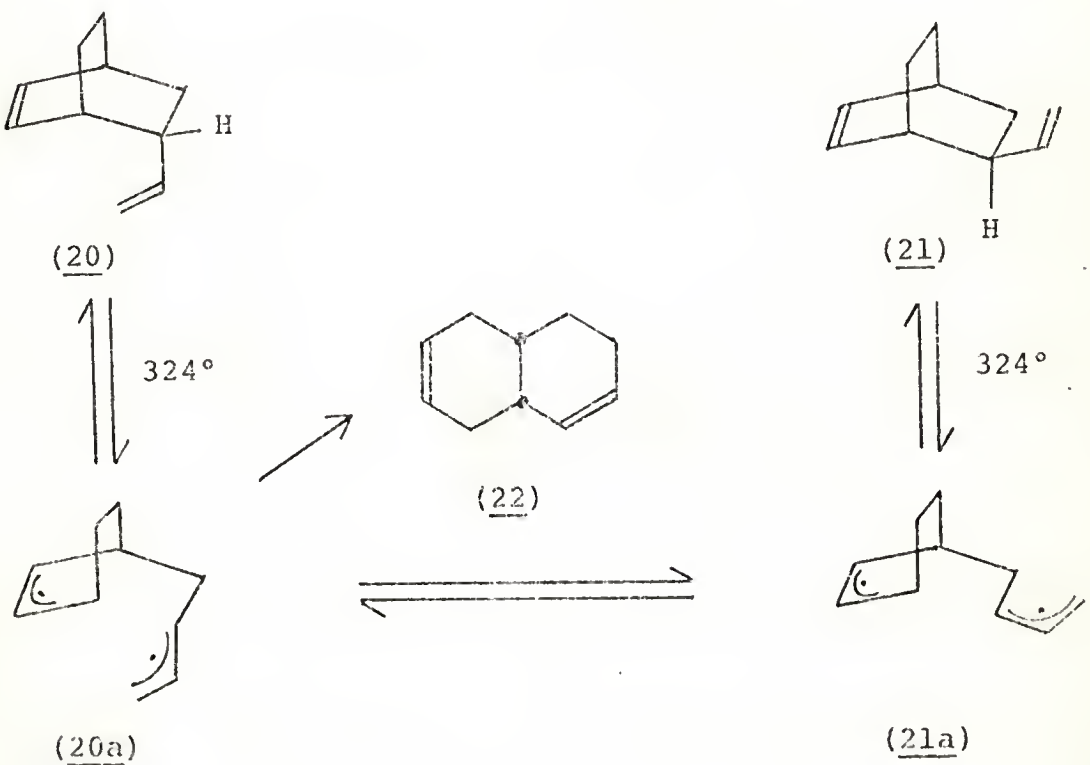


70% 20% 4%

(16) (17) (18) (15) (19)

by diradical (17) and/or by cis-trans isomerization from diradical (17) to cis-1,2-divinylcyclobutane (14) which then under the reaction conditions would proceed smoothly to (15) via a concerted Cope rearrangement. The most simple mechanistic rationalization would invoke the diradical intermediate (17) as the major pathway with the concerted [3,3]-sigmatropic rearrangement being preempted for geometric reasons.

Similarly, Berson and Walsh examined the pyrolytic behavior of endo- and exo-2-vinylbiclo[2.2.2]oct-5-ene (20 and 21 respectively).[13] The endo-vinyl epimer (20) could undergo transformation to cis-$\Delta^{1,6}$-hexalin (22) through either a concerted [3,3]-sigmatropic migration or through biradical (20a). However, the Cope rearrangement was geometrically inaccessible to the exo-vinyl epimer (21),



(20) (21) (22) (20a) (21a)

so that the biradical (21a) pathway became an energetically attractive alternative for transformation to (22). Competition experiments showed that the rates for overall disappearance between (20) and (21) over an 80° temperature range were nearly identical and gave a $\Delta\Delta H^{*}$ of only 1.8±1.5 kcal/mol with the exo-vinyl compound (21) apparently having the lower ΔH^{*}. The authors felt that the data argued against a concerted Cope rearrangement for either (20) or (21) and were most simply explained in terms of a stepwise mechanism passing through diradical intermediates.

Lastly, secondary deuterium isotope effect studies have been utilized in recent years by physical organic chemists to test the simultaneity or lack of it in pericyclic reactions, such as the thermal Cope rearrangement.[14]

What makes isotope effects unique and particularly attractive as a mechanistic probe is that the potential energy surfaces, unlike substituent effects, for isotopic isomers are identical. This would imply that the origin of isotope effects is of a vibrational, nonelectronic nature. It was found that for hydrogen isotopes, where vibrational frequencies and, therefore, zero point energies are large, that the major contribution to isotope effects stems from zero point vibrational energy differences. This simplification arises because all vibrations which involve hydrogen and its isotopes would essentially remain, at ordinary temperatures, in their lowest (zero point) energy levels.[14, 15] Indeed, the zero point energy level would

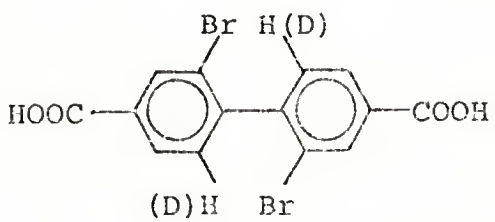
always be less for D (or C-D) than for H (or C-H) vibrations.[15]

Observation of secondary deuterium isotope effects have been correlated with steric interactions,[16] inductive[15, 17] and hyperconjugative[18] effects, and rehybridization changes,[19] dependent upon which concept clarified the experimental data best. These points of view, although somewhat misleading, are interpretations of vibrational force constant or zero point energy changes. Yet, they have allowed the practicing chemist to discuss isotope effects in the same familiar language that is commonly used to discuss substituent effects, although the latter have an electronic origin. So too, it allows reasonable qualitative predictions to be made with regard to sign and magnitude of vibrational force constant changes in an isotope effect study as a preliminary to quantitative measurements.

Because thermal reorganizations of small carbocycles generally involve little if any charge separation and usually proceed either through a synchronous or a diradical pathway, a steric interpretation would appear to offer the most useful clarification and rationalization of any deuterium isotope effect study. Indeed, through the harmonic approximation employed by Bartell,[16b, 16c] a one to one correspondence between steric and vibrational force constant changes can be made. Thus, a steric approach might suggest independent predictions of the potential

energy surfaces of hydrogen isotopes in a systematic fashion.

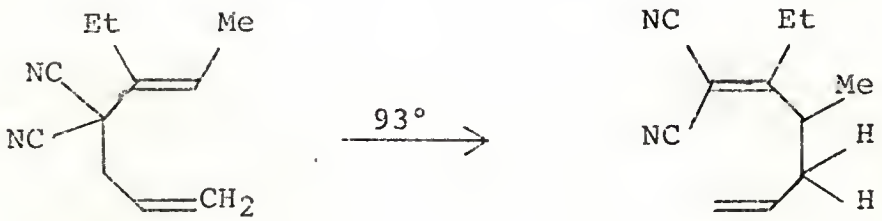
A steric interpretation of hydrogen isotope effects derives from the smaller amplitude and effective size of D, so that it has less of a steric requirement than H.[15] This is purely a vibrational phenomenon, since the more sterically crowded a C-H bond is, the greater will be the vibrational frequencies, especially the out-of-plane bending frequencies, associated with that bond.[14] Thus, on going from reactant to a transition state which is sterically more congested, the rate of reaction for the protio isomer k_H should be less than the rate of reaction for the deuterio isomer k_D, and an inverse isotope effect ($k_H/k_D < 1$) should result. If there is less steric congestion from reactant to transition state, then a normal isotope effect ($k_H/k_D > 1$) ought to result. A good case in point was the racemization of compound (23).[16a]



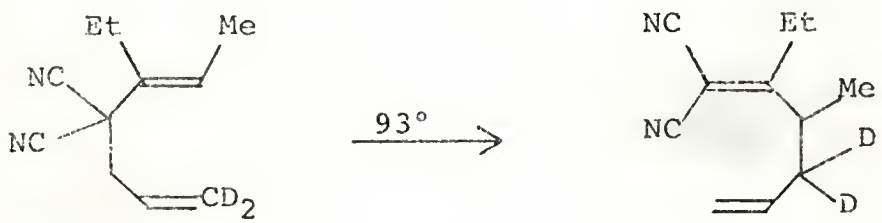
(23)

The reaction has a high activation energy with a planar transition state,[20] so that sizeable van der Waals interactions between adjacent H and Br are present. On steric grounds, an inverse isotope effect would be expected and in fact was observed ($k_H/k_D = 0.84 \pm 0.03$).

In the Cope rearrangement, both kinetic and thermodynamic deuterium isotope effect studies have been probed in some detail. When a kinetic deuterium isotope effect was measured at the bond-making site for the thermal [3,3]-sigmatropic transformation of the substituted 1,5-hexadiene (24 vs. 24-d_2), an inverse kinetic isotope effect (k_H/k_D = 0.94±0.02) resulted.[21] In this case,



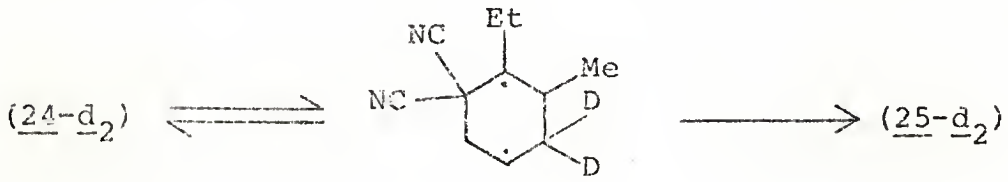
(24) (25)



(24-d_2) (25-d_2)

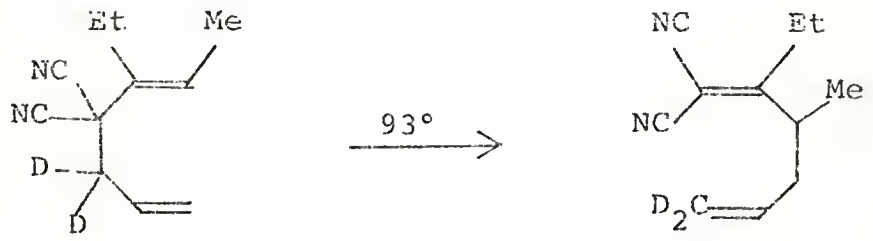
the sp^3 carbon bearing H has significantly higher C-H bending vibrations associated with it than for an sp^2 carbon.[14] Thus, as the migration in (24) proceeds through a cyclic multicentered transition state, the sp^2 carbon at C-6 becomes more sp^3-like, so that the steric requirement of H attached at the more crowded tetrahedral geometry of an sp^3 position compels (24) to rearrange more reluctantly

to (25) than (24-d_2) to (25-d_2). However, this inverse kinetic isotope effect could also be rationalized by invoking a two-step mechanism involving the diradical intermediate (26). To resolve this ambiguity, the



(26)

kinetic deuterium isotope effect was also determined at the bond-breaking site by comparing the rates of rearrangement of (24) with the suitably labeled (24'-d_2). At



(24'-d_2) (25'-d_2)

93° a normal isotope effect of 1.19±0.03 was observed.[21] The combination of these two isotope effects precluded the two-step mechanism as a viable alternative and reinforced other corroborative experiments, demonstrating the concertedness of the thermal rearrangement of acyclic 1,5-hexadienes.[2] These two transformations were practically irreversible which reflected the greater stability of the product (ΔH = -5 kcal/mol), so that the transition state should be more reactant- than product-like.[22] Because

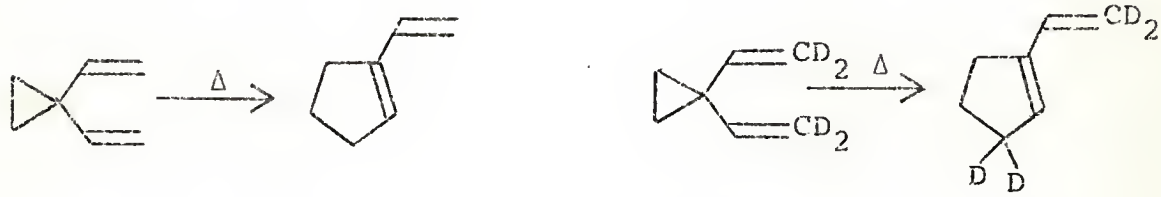
of the proportionately larger kinetic isotope effect at the bond-breaking site, is bond-breaking farther along than bond-making? The authors argued that force constant changes are nonlinear functions along the reaction coordinate. This is supported by theoretical calculations.[23] Thus, with a relatively small increase in C-C bond distance, a relatively sharp decrease in the force constant would ensue. Likewise, as the two atoms approach one another in the bond-forming process, a small increase in the force constant should not be an unlikely expectation.

More frequently thermodynamic secondary deuterium isotope effects have been encountered in Cope rearrangements.[24] The degenerate nature of many of the systems studied precluded any possible measurement of a kinetic isotope effect. The thermal equilibrium of labeled biallyl (27) was observed. Based on previous arguments,

(27a) (27b)

where D can better accomodate a more sterically congested environment, D would be expected to accumulate preferentially at the tetrahedral orientation of the isotopically substituted carbons. The product ratio (27a/27b) of 0.81±0.02 was consistent with expectations.[25]

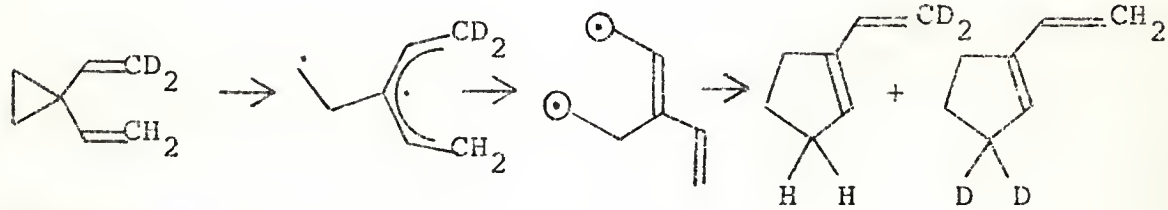
The thermal rearrangement of 1,1-divinylcyclopropane (1) to vinylcyclopentene (28) does not involve a [3,3]-sigmatropic or Cope process. Nevertheless, the kinetic isotope effects ascertained are enlightening and suggestive. Both intermolecular and intramolecular kinetic isotope effects were determined. The former (k_H/k_D = 1.08±0.07) compares the rates of reaction of



(1) (28) (1-d_4) (28-d_4)

(1) with (1-d_4) and reflects the force constant changes in the rate-determining step.[1] Had the above transformation been a concerted [1,3]-sigmatropic process, an inverse isotope effect should result, because the overall transformation involves the conversion of the hydrogen isotopes from a trigonal to the more crowded tetrahedral orientation at the carbon of the product. A diradical mechanism can justify this normal isotope effect, regardless of whether the rate-determining step involves biradical formation through ring cleavage or biradical destruction. If the former, ring cleavage creates new torsional modes which favor H over D.[26] Moreover, since ring cleavage requires the transformation of the isotopically labelled site from sp^2 to sp^2-radical,

experimental analogy indicates that such a transformation should be accompanied by a small but normal isotope effect.[27] For biradical destruction, Dolbier and Alonso observed a normal intramolecular isotope effect ($k_H/k_D = 1.12 \pm 0.02$).[1] It was determined from the product ratio (28a/28b) in the thermolysis of (1-d_2). If an



(1-d_2) planar nonplanar (28a) (28b)

inverse intramolecular isotope effect were observed in biradical destruction, the bulk of the activation energy would be associated with ring closure in which the sp^2-radical becomes transformed to the more crowded sp^3 position of the product. However, observation of a small but normal isotope effect demanded that isotopic discrimination be associated with the twisting of a terminal methylene group from its planar to its nonplanar configuration, with concomitant destruction of π-bonding at the terminus. Considering that the CH_2 group has a relatively higher zero point energy than a CD_2 group, it requires a relatively lower activation energy for this twisting motion to the nonplanar pentadienyl form, that is, the CH_2 group has a head start in surmounting the energy barrier for rotation because of its relatively smaller

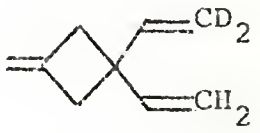
moment of inertia. Thus, the predicted preference for the CH_2 twisting motion is observed upon examination of the product ratios where (28a) > (28b).

Had the rearrangement of (1) to (28) been concerted, bond-breaking and bond-making would have a common transition state, so that an inverse isotope effect would also be expected. Thus, despite the near identity of the two isotope effects, the fact that they are normal, demands that biradical intermediates be involved. With both isotope effects being the same within experimental error, it could be construed that biradical destruction is rate-determining. However, it could also be construed that the two isotope effects could each be associated with a different step in the mechanistic pathway leading to product and are fortuitously the same.

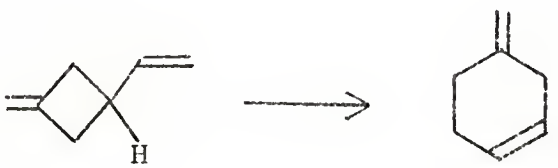
A secondary deuterium isotope effect study on the pyrolysis of a 1,5-hexadiene involving prior ring cleavage has not been unambiguously examined.[28] In conjunction with activation parameters, a secondary deuterium isotope effect study on the thermal conversion of (2) to (3) might allow distinction between mechanisms. This would entail a determination of both inter- and intramolecular isotope effects. The former involves comparison of the rate ratio of (2) with (2-d_4). The latter can be ascertained from the product ratio upon thermolysis of (2-d_2). Determination and comparison of the activation parameters for methylene-3-vinylcyclobutane (29) to

4-methylenecyclohexene (30) with those determined from pyrolysis of (2) would also allow insight into the mechanism for rearrangement.

(2-d_4)



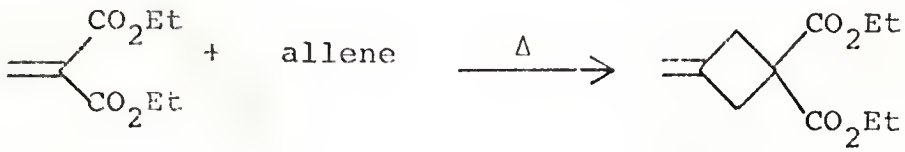
(2-d_2)



(29) (30)

RESULTS

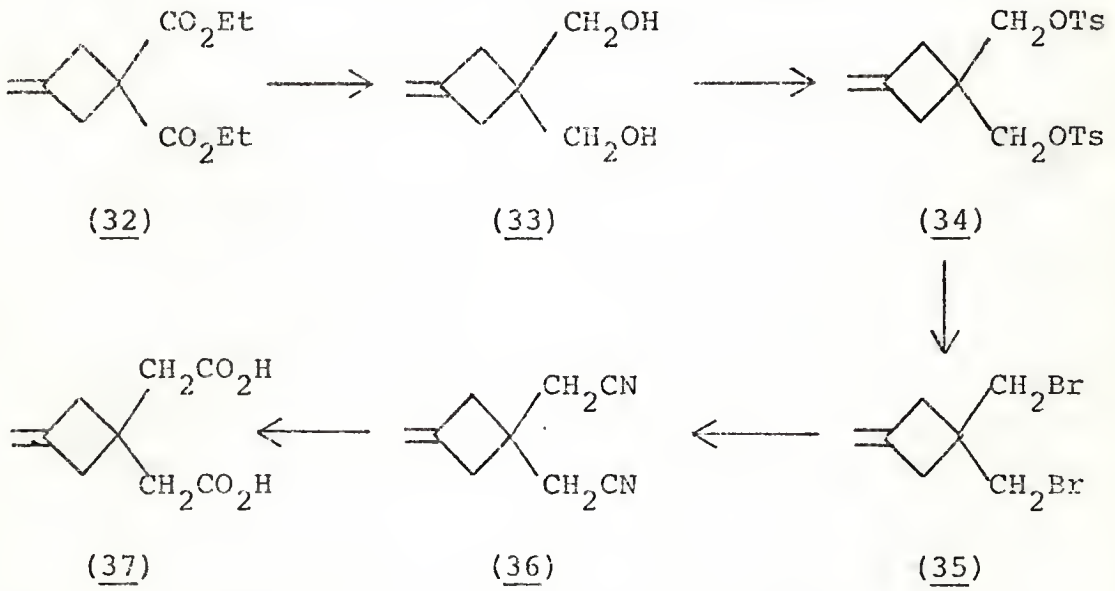
Multistep syntheses were employed to construct the novel isotopic isomers (2), (2-d_4), and (2-d_2) as well as the analogous methylene-3-vinylcyclobutane (29). Because unambiguous, well-documented reaction types were employed, product identification was considerably simplified. Efficient construction of a cyclobutane system generally requires either (a) the alkylation of active methylene compounds by, for example, 1,3-dibromopropane[29] or (b) a thermal [2 + 2]-cycloaddition under autogenous pressure in a "bomb" reaction. The synthetic feasibility of the latter has been demonstrated particularly with the cycloaddition of allene to active ethylene compounds.[30] This entry into substituted methylenecyclobutanes prompted the preparation of diethyl-3-methylene-1,1-cyclobutanedicarboxylate (32) by cycloaddition of methylenediethylmalonate (31) with allene in an analogous fashion.



(31) (32)

The reaction of acrylonitrile with allene is well known, and from it (29) can be prepared.[30]

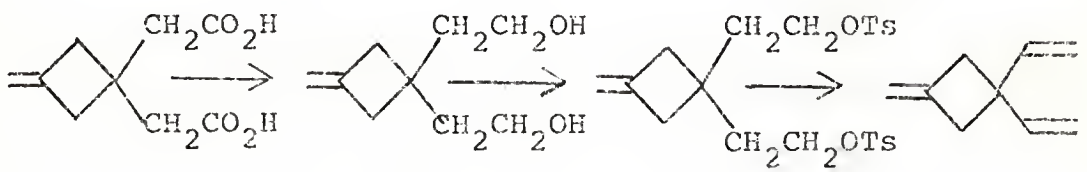
The common precursor to (2), (2-d_4), and (2-d_2) was 3-methylenecyclobutane-1,1-diacetic acid (37) which was prepared according to the scheme depicted below.



The 3-methylenecyclobutane-1,1-dimethanol (33) was conveniently prepared by $LiAlH_4$ reduction of (32). Bis-tosylation of diol (33) produced (34) which was converted in high yield to 1,1-bis(bromomethyl)-3-methylenecyclobutane (35) by treatment with LiBr in refluxing anhydrous acetone. The ditosylate (34) could have been directly converted to 3-methylene-1,1-diacetonitrile (36); however, the literature indicated that such a reaction would involve some decomposition, and the reaction product would be difficult to work up.[31] Reaction of the dibromide (35) with KCN in DMSO at 85° for approximately 2 days produced

in 87% yield the expected diacetonitrile (36). Hydrolysis of this product afforded the diacetic acid (37). Nmr spectroscopy indicated the characteristic triplet (ring-allyl H) and pentet (exocyclic-methylene H) splitting pattern (J = 2.5 Hz) for all these compounds. Confirmation by ir and mass spectra and by elemental analyses completed product identifications, and all were consistent with their proposed product structures.

From the 3-methylenecyclobutane-1,1-diacetic acid (37), 1,1-divinyl-3-methylenecyclobutane (2) was prepared. This

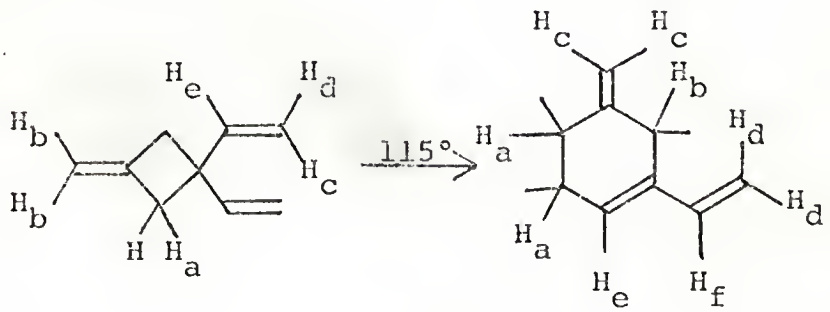


(37) (38) (39) (2)

was accomplished by $LiAlH_4$ reduction of the diacetic acid (37), yielding the diol (38), which was easily converted to the ditosylate (39). Bisdehydrotosylation was effected in 20% yield by treatment of an anhydrous DMSO solution of ditosylate (39) with solid potassium-t-butoxide at 25° under full vacuum. The volatile products were condensed in a coiled trap, cooled by liquid nitrogen. Separation was effectively accomplished on a 5' (18%) DC-200 column at 55°. The structure of (2) was verified by nmr, ir, and mass spectroscopy and by elemental analysis. The 100 MHz nmr (see Figure 10) showed a triplet at δ 2.75 ($4H_a$, J_{ab} = 2.7 Hz), a pentet at 4.82 ($2H_b$, J_{ab} = 2.7 Hz), and a

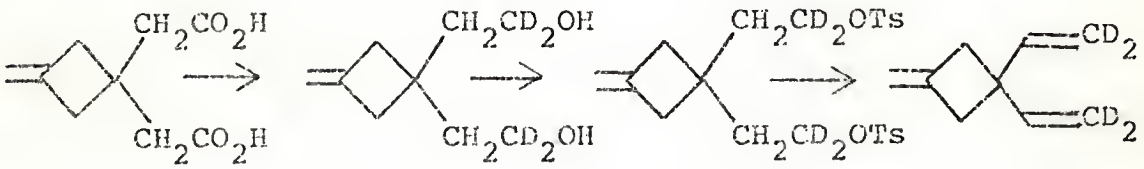
fourteen-line[32] ABX pattern for the divinyl region which has chemical shifts at 5.01 ($2H_c$, J_{cd} = 1.4 Hz, J_{ce} = 16.6 Hz), 5.06 ($2H_d$, J_{cd} = 1.4 Hz, J_{de} = 10.2 Hz), and 6.03 ($2H_e$, J_{ce} = 16.6 Hz, J_{de} = 10.2 Hz); its ir spectrum (see Figure 12) showed bands at 3045, 2995, 2960, 1640, 1415, 1220, 994, 880 cm^{-1}.

The compound (2) was smoothly converted to 4-methylene-2-vinylcyclohexene (3) at 115° in a dilute solution of either n-decane, benzene, or CCl_4 using sealed tubes. The conversion appeared to be quantitative and clean. Both structure and purity of (3) were confirmed by nmr, ir, and mass spectroscopy as well as by elemental analysis. Its nmr (see Figure 13) bore similarities to the known 4-methylene-cyclohexene (30)[33] and showed broad singlets at δ 2.30 ($4H_a$) and 2.85 ($2H_b$), multiplets at 4.55-5.20 ($2H_c$ + $2H_d$), 5.52-5.85 ($1H_e$), and an AB quartet at 6.28 ($1H_f$, J_{trans} = 17 Hz, J_{cis} = 10 Hz); its ir (see Figure 14) showed bands at 3090, 3070, 3000, 2980, 2960, 2910, 2835, 1650, 1638, 1605, 1430, 1335, 1220, 975, 890, 840 cm^{-1}; its uv exhibited a λ_{max} at 230 nm (ε 22,200).



(2) (3)

Preparation of (2-d_4) was accomplished by a similar route, where isotopic labelling was introduced in the reduction of the diacetic acid (37) with $LiAlD_4$. Bis-dehydrotosylation afforded a 17% yield of (2-d_4). The

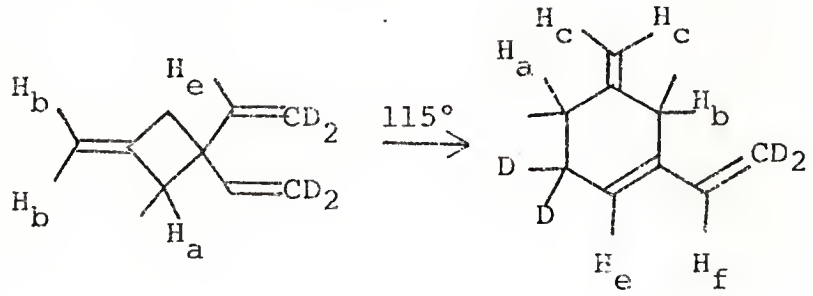


(37) (38-d_4) (39-d_4) (2-d_4)

structure of (2-d_4) was verified by nmr, ir, and mass spectroscopy and by elemental analysis. Its nmr (see Figure 15) revealed a triplet at δ 2.72 ($4H_a$, J_{ab} = 2.5 Hz), a pentet at 4.89 ($2H_b$, J_{ab} = 2.5 Hz), and a multiplet at 5.85-6.10 ($2H_e$); its ir (see Figure 16) exhibited bands at 3090, 3010, 2970, 2935, 2320 (w), 2230 (w), 1680, 1600, 1420, 1035, 945, 880, 735 cm^{-1}. Mass spectral analysis (15 ev) was used to establish its isotopic purity at 99.8%.

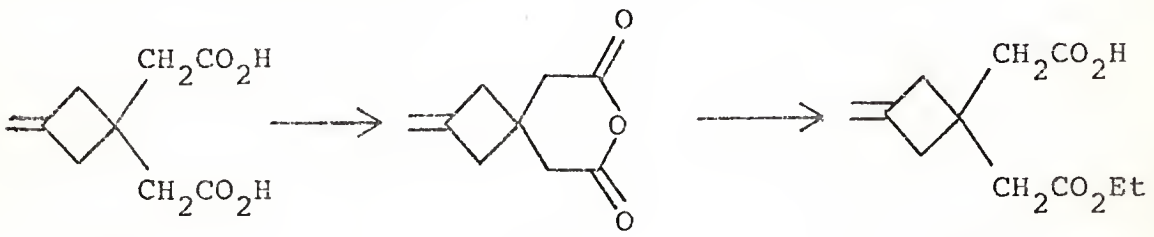
The thermal reorganization of (2-d_4) to (3-d_4) was accomplished in a sealed tube, the sample diluted with benzene. Glpc analysis on a 5' (18%) DC-200 column at 60° and 110° indicated that only the expected (3-d_4) appeared to have formed. Both its structure and its isotopic purity were confirmed by nmr, ir, mass (15 ev) spectroscopy, and elemental analysis. Its nmr (see Figure 17) showed broad singlets at δ 2.26 ($2H_a$), 2.82 ($2H_b$), 5.71 ($1H_e$), as well as multiplets at 4.67-4.86 ($2H_c$) and at 6.15-6.36 ($1H_f$); its ir (see Figure 18) showed bands at 3080, 2990, 2930,

2860, 2190 (w), 2160 (w), 2100 (w), 1680, 1650, 1445, 1070, 1030, 945, 890, 718 cm^{-1}.

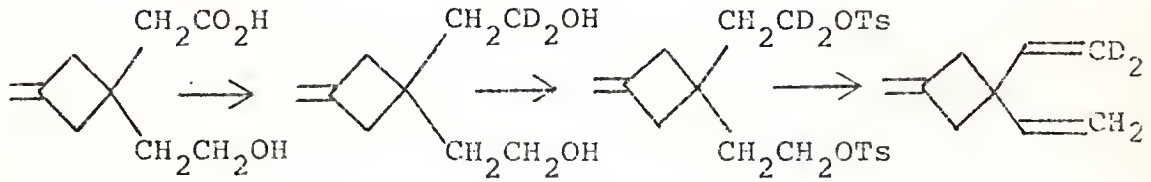


(2-d_4) (3-d_4)

The synthesis of the novel 3-methylene-1-vinyl-1-(vinyl-2,2-d_2)cyclobutane (2-d_2) was accomplished in six steps from the 3-methylene-1,1-diacetic acid (37).



(37) (40) (41)



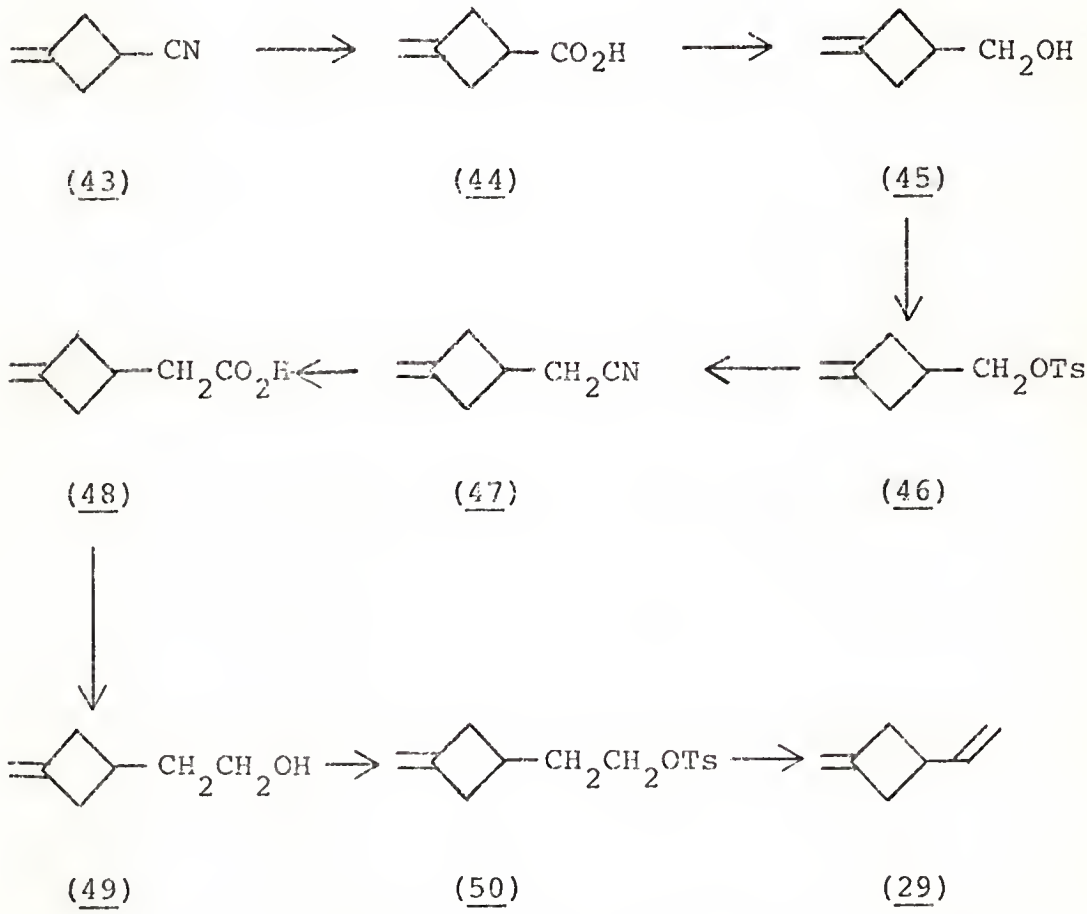
(42) (38-d_2) (39-d_2) (2-d_2)

Dehydration of the diacetic acid (37) with refluxing acetic anhydride quantitatively produced the cyclic anhydride (40). Heating of (40) for 2 hr in the presence of absolute ethanol cleanly produced the difunctional half-ester, half-acid (41) in high yield. The key step, however, was the

Bouveault-Blanc reduction[34] of the carboxylate function with sodium metal in absolute ethanol and liquid NH_3. At this point, (42) could be reduced with $LiAlD_4$ to introduce deuteriums in the diol (38-d_2) which was subsequently converted to the ditosylate (39-d_2). The ditosylate (39-d_2) when treated with potassium-t-butoxide in a DMSO solvent resulted in the product (2-d_2) whose nmr, ir, and mass spectra were entirely consistent with its structure. Its nmr (see Figure 19) showed a triplet at δ 2.87 (4H, J = 2.5 Hz), and multiplets at 4.82-5.18 (3H), 5.21-5.38 (1H), and at 5.92-6.12 (2H); its ir (see Figure 20) showed strong bands at 3090, 3010, 2975, 2940, 2280 (w), 2130 (w), 1680, 920, 880 cm^{-1}. Mass spectral analysis (6 ev) was used to establish its exact isotopic isomer distribution: (2-d_2), 0.861; (2-d_3), 0.050; (2-d_4), 0.089.

In an analogous fashion, methylene-3-vinylcyclobutane (29) was prepared in an eight-step sequence from 3-methylenecyclobutanecarbonitrile (43). Both (43) and (44) are known in the literature.[31] Structures for the other compounds in this sequence were verified by their nmr, ir, and mass spectra. All were produced in high yield except the dehydrotosylation step which afforded (29) in only 20% yield. The structure of (29) was confirmed by its nmr, ir, and mass spectra. Elemental analysis indicated its high purity. The nmr (see Figure 23) showed multiplets at δ 2.33-3.12 ($5H_a$), 4.65-4.95 ($2H_b + 2H_c$), 4.97-5.18 ($1H_d$),

and 5.80-6.40 ($1H_e$); its ir (see Figure 24) had bands at 3090, 2950, 1680, 1645, 1420, 990, 920, 915, 880 cm^{-1}.

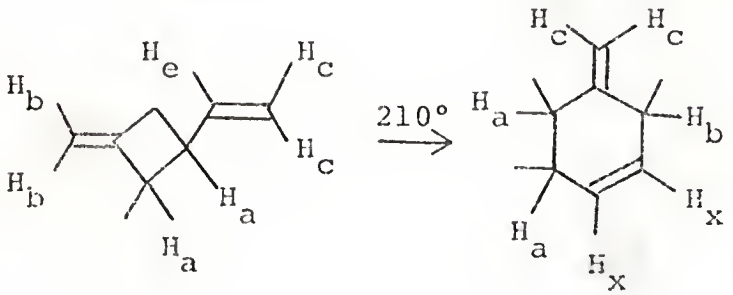


(43) (44) (45)

(48) (47) (46)

(49) (50) (29)

In addition, the structure of (29) was confirmed by its smooth thermoreorganization to the known 4-methylenecyclohexene (30) whose spectral characteristics were nearly



(29) (30)

identical to those reported in the literature.[33] For reference, the nmr (see Figure 25) for (30) showed broad singlets at δ 2.21 ($4H_a$), 2.72 ($2H_b$), 4.68 ($2H_c$), and 5.62 ($2H_x$).

Activation energy parameters for the thermolysis of (2) and (29) were determined. The rate of disappearance of (2) in an n-decane solution with respect to n-nonane as an internal standard was followed on a Hewlett-Packard model 5710A gas chromatograph with flame ionization detector. The gas chromatographic analyses were performed on a 7.5' (2%) DC-200 column at 56°. The chemical composition of the kinetic samples was determined with a Vidar Autolab 6300 digital integrator to facilitate and minimize the error in determining relative peak areas. A first-order, least squares program was used in conjunction with a pdp 8/e digital computer to analyze all the data on a concentration versus time plot as a correlation coefficient where 1.000 is the optimum fit for this unimolecular reaction. Rate constants at seven different temperatures in the range of 86.1° to 121.1° were determined and compiled in Table 1. An Arrhenius plot was constructed from the data in terms of providing Arrhenius parameters. For (2), the appropriate parameters were determined: energy of activation, 27.27±0.30 kcal/mol; log A, 11.87±0.17; enthalpy of activation, 26.53±0.30 kcal/mol at 103.2°; entropy of activation, -6.66±0.78 cal/mol-deg at 103.2°;

free energy of activation, 29.03±0.78 kcal/mol at 103.2°.

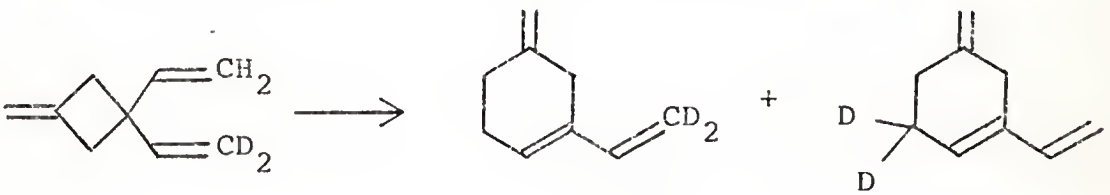
The rate of disappearance of (29) in an n-decane solvent was followed also by the use of a Hewlett-Packard model 5710A gas chromatograph with flame ionization detector but without the need for an internal standard. In every other respect, the analysis, the treatment of the data, and the determination of the activation parameters for the thermoreorganization of (29) were identical with that for the thermolysis of (2). Rate constants at six different temperatures in the range of 175.0° to 211.0° were determined and compiled in Table 6. An Arrhenius plot was constructed in Figure 5. Computer evaluation of the data provided the following activation parameters: energy of activation, 35.67±0.41 kcal/mol; log A, 12.70 ±0.19; enthalpy of activation, 34.74±0.41 kcal/mol at 192.3°; entropy of activation, -3.29±0.87 cal/mol-deg at 192.3°; free energy of activation, 36.28±0.87 kcal/mol at 192.3°.

These results indicate that the addition of a second vinyl group in the ring system lowers the activation energy necessary for rearrangement by about 8 kcal/mol.

The intermolecular isotope effect (k_H/k_D) was obtained from the ratio of rate constants of (2) and (2-d_4). The analysis and treatment of the data were as previously described and detailed in the experimental section. At a particular temperature, the kinetic pyrolysis of (2-d_4) was performed immediately after the kinetic pyrolysis of (2). At 99.9°, the intermolecular isotope effect (k_H/k_D)

was 1.05±0.03 and, at 121.1°, the (k_H/k_D) ratio was 1.04±0.03. Within experimental error, the results indicate that the intermolecular isotope effect was not temperature dependent. The rate ratio was recalculated at each temperature by adding the standard error associated with the rate constant for (2) and by subtracting the standard error associated with the rate constant for (2-d_4). The deviation of this rate ratio from that determined above is quoted as the error in the intermolecular isotope effect.

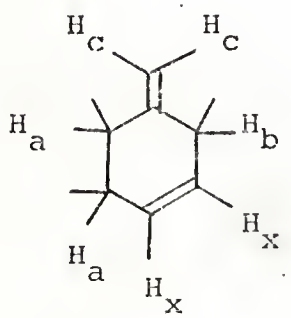
An intramolecular isotope effect (k_H/k_D = 3a/3b = 1.14±0.07) was obtained by pyrolysis of a dilute benzene solution of (2-d_2) at 121.1° for 5 hr. A sample of (2) was subjected to the same conditions and used as a control.



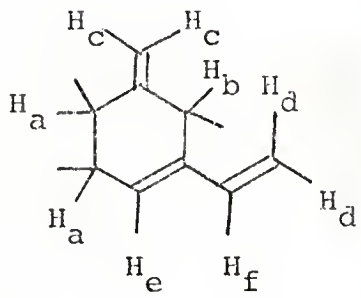
(2-d_2) (3a) (3b)

Determination of the intramolecular isotope effect was based upon nmr integration ratios of the purified mixture of (3a) and (3b). Two separate determinations were possible from a 100 MHz nmr spectrum (see Figures 21 and 22). One involved the continuous-sweep integrations of the aliphatic region with the determination of the ratio of the allylic H/diallylic H or H_a/H_b. The other involved the continuous-sweep integrations of the vinylic region with the

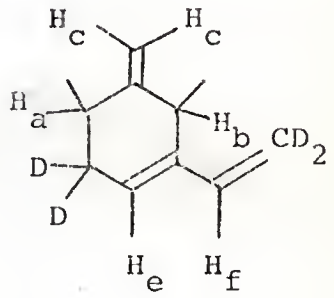
determination of the ratio of the terminal-vinyl H/ vinyl-ring H or $(H_c + H_d)/H_e$. The paucity of the sample only allowed the determination of the ratio of (3a/3b) present from a single nmr sample. As a result, the reported error was maximized. The nmr integration ratio for each region (aliphatic or vinylic) was recalculated by adding the standard error associated with the nmr integration ratio and also by subtracting the standard error asscciated with the same integration ratio. Thus, from the high, low, and mean values of the nmr integration ratio, three intramolecular isotope effect values were determined for each region. The average and standard deviation of each set of three values is the reported isotope effect for each region. Thus, two values for the intramolecular isotope effect, one for each reagion, were determined. Their average is the reported as the final value for the intramolecular isotope effect.



(30)



(3)



(3-d_4)

Assignment of the protons in (3) merits some attention. Protons H_a at δ 2.30 are monoallylic and relative to the other hydrogens should be upfield. For the reported 4-methylenecyclchexene (30),[33] the monoallylic hydrogens are found at δ 2.21 (lit. 2.1). Moreover, the integral signal at δ 2.26 for the nmr of (3-d_4) decreased by one-half, as expected when half the monoallylic sites are deuterated. The protons H_b at δ 2.85 are diallylic and somewhat downfield from H_a. When half the monoallylic positions are deuterated as in (3-d_4), the nmr integral signal for the diallylic protons should and does increase twofold relative to H_a. Thus, δ 2.85 was assigned to H_b. The protons H_c and H_d at δ 4.55-5.20 are not readily distinguishable from one another in the sense that their integration values cannot be separated. Intuition tells us that the chemical shifts for these hydrogens should vary little from those same kinds of hydrogens in (2). Moreover, the nmr spectrum for (30) reveals a broad singlet at δ 4.68 (lit. 4.7)[33] for the exocyclic vinylic CH_2, and the nmr spectrum for (3-d_4), where no terminal vinylic CH_2 is present, shows an unresolved multiplet at δ 4.67-4.86 for its exocyclic vinylic CH_2. Comparative inspection with the nmr of (2) reveals that the terminal vinylic CH_2 was always slightly downfield from the exocyclic vinylic CH_2. Similarities in the nmr of (2) and (3-d_4) suggest that the AB quartet in (3) be assigned to δ 6.28 as H_f. By default the signal at δ 5.52-5.85 was assigned to H_e.

DISCUSSION

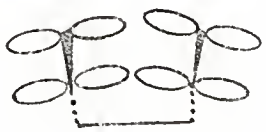
For the thermal reorganization of 1,1-divinyl-3-methylenecyclobutane (2) to 4-methylene-2-vinylcyclohexene (3) and methylene-3-vinylcyclobutane (29) to 4-methylenecyclohexene (30), three distinct mechanistic pathways can be envisioned: (a) a concerted [1,3]-sigmatropic rearrangement, (b) a concerted [3,3]-sigmatropic or Cope rearrangement, and (c) a multistep process involving diradical intermediates.

Of the three alternatives, pathway (a) seems least likely. There are but few examples of the concerted [1,3]-sigmatropic process. The thermal and stereospecific transformation of endo-5-methylbicyclo[2.1.1]hex-2-ene (and related derivatives) with inversion of configuration to exo-6-methylbicyclo[3.1.0]hex-2-ene suggests a concerted suprafacial 1,3 alkyl shift.[35] More often cited is the work by Berson and coworkers on the thermal conversion of exo-7-deuterio-endo,cis-bicyclo[3.2.0]hept-2-enyl-6-acetate to exo-3-deuterio-exo-5-norbornenyl-2-acetate which also proceeds with inversion of configuration at the migrating center.[36] However, both cases appear to exemplify the need for two geometric requisites: (a) relief of ring strain, and (b) a π-bond center held rigidly near to the migrating

σ-bond to allow the occurrence of the suprafacial 1,3 shift. The latter can be achieved by ring fusion, and yet it is absent in the much studied thermal reorganization of vinylcyclopropane, despite its considerable ring strain energy (27.6 kcal/mol),[37] to cyclopentene. The observed activation energy of 49.7 kcal/mol[38] can be reasonably accounted for by a diradical intermediate with a full complement of allylic stabilization energy. Experimental evidence obtained in a study of specifically deuterium labelled vinylcyclopropanes supports the concept of a diradical pathway for this rearrangement.[12b] Rate and stereochemical product studies on trans-1,2-dialkenylcyclobutanes,[10, 39] which are structurally more related to the nature of our research interests here, also suggested a lack of concert in their ring expansion to vinylcyclohexenes. The lack of a geometric lock on the π-bond center adjacent to the potentially migrating σ-bond may be the significant factor responsible for the lack of concert in these nonfused systems. The same feature is also lacking in the analogous methylene-3-vinylcyclobutanes (2) and (29), and with the preponderant lack of analogy no further comment on the concerted [1,3]-sigmatropic shift seems appropriate. The mechanistic picture then for the thermal rearrangement of (2) and (29) is somewhat clarified, and attention is thereby focused on the two remaining pathways (b) and (c).

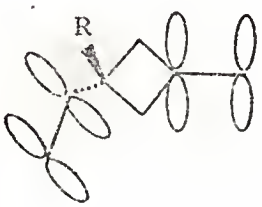
As noted earlier, in the Cope rearrangement either a four-centered chair (9) or a six-centered boat (10)

conformation is attained in its cyclic transition state. It appears essential that for the thermally activated concerted reaction of 1,5-hexadienes, considerable overlap must be developed between the π-orbitals at C-1 and C-6 as the 3,4 σ-bond breaks. For those Cope reactions that are irreversible and exothermic, the transition state should resemble the reactant more than the product geometry.[22] Hence, comparison of ground state models of acyclic 1,5-hexadienes with the related methylene-3-vinylcyclobutanes (2) and (29) is instructive. Unquestionably, the ground state boat (52) and the ground state chair (53) conformations of the acyclic 1,5-hexadienes can easily achieve substantial orbital overlap between C-1 and C-6 as the 3,4 σ-bond breaks along the



(52)

(53)



(2) R = $CH=CH_2$

(29) R = H

reaction coordinate. However, inspection of the geometric orientation of the π-bond centers in the methylene-3-vinylcyclobutanes (2) and (29) reveals that an unbearably high angle strain would be required in the transition state for development of sufficient 1,6 orbital overlap for concert

in their thermal transformations. Indeed, the alternative involves strain free diradical intermediates which appear much more attractive.

One of the well-established features of the Cope reaction is the characteristically high negative entropy of activation which reflects the well-ordered cyclic multicentered transition state for the rearrangement. Values more or less center around -10 eu to -14 eu for four-centered reactions[2] and appear to be even more negative for six-centered reactions. Since entropy of activation ΔS^* and frequency factor A are related by the equation, $\Delta S^* = R\ln(Ah/ekT)$,[40] Benson and O'Neal have indicated that the vast majority of four-centered Cope reactions fall within the narrow A factor range of $10^{13.5\pm1.0}$ sec^{-1}, and for six-centered reactions a range of $10^{11.5\pm1.5}$ sec^{-1} has been ascertained.[41] High A factors ($10^{14.0\pm1.0}$ sec^{-1}) and positive or nearly zero ΔS^* values are generally anticipated for diradical reactions, since few steric restrictions are imposed on their transition states.[42] Moreover, when diradicals are borne through ring cleavage, new rotational and torsional modes are generated, and an entropy gain is expected. Albeit rather low ΔS^* values and low A factors were observed in the pyrolysis of 1,1-divinyl-3-methylenecyclobutane (2) to 4-methylene-2-vinylcyclohexene (3) and methylene-3-vinylcyclobutane (29) to 4-methylenecyclohexene (30) for the former $\Delta S^* = -6.7$ eu and $A = 10^{11.9}$ sec^{-1} and for the latter

ΔS^* = -3.3 eu and A = $10^{12.7}$ sec^{-1}. This may seem surprising. How then can these low values be rationalized in terms of a multistep process involving diradical intermediates? It must be noted that in the reactants (2) and (29) the vinyl groups can undergo internal rotations, whereas if a biradical resulted the two conjugated groups cannot. For example, a biradical pathway has been unambiguously established for the well-known vinylcyclopropane to cyclopentene rearrangement.[12] One of the steric requirements for allylic stabilization is that all seven atoms (three carbons and four hydrogens) should be in the same plane. Compared to the ground state, there has been considerable reduction in the internal rotations of the vinyl group. Correspondingly lower values (ΔS^* = -0.3 eu, A = $10^{13.5}$ sec^{-1})[38] were observed for the pyrolysis of vinylcyclopropane over that for either the isomerization of cis-1,2-dideuteriocyclopropane (ΔS^* = 12.8 eu, A = $10^{16.4}$ sec^{-1})[43] or the decomposition of 1-ethylcyclopropane to 1-pentene (ΔS^* = 3.6 eu, A = $10^{14.4}$ sec^{-1}),[44] depending upon which model serves better for comparison. Similarly, rearrangement of vinylcyclobutane to cyclohexene should occur with a lower ΔS^* and a lower A factor over that for either the isomerization of cis-1,2-dideuteriocyclobutane or the decomposition of ethylcyclobutane. Unfortunately, data are not available for the former two pyrolyses. However, the isopropenylcyclobutane to 1-methylcyclohexene rearrangement

(ΔS^* = 4.6 eu, A = $10^{14.5}$ sec^{-1})[45] can be conveniently compared to the decomposition of isopropylcyclobutane to ethylene and 3-methyl-1-butene (ΔS^* = 9.3 eu, A = $10^{15.6}$ sec^{-1}),[46] provided that the rate-determining step of the latter involves ring cleavage in diradical formation. The reduction in ΔS^* and A factor values with the formation of allyl radicals has been noted by Frey in his review on the pyrolyses of small ring compounds from which other similar correlations can be made.[11]

Our kinetic results fit rather nicely into the above picture, if diradical intermediates intervene in these thermal reorganizations. The low ΔS^* (-3.3 eu) and low A factor ($10^{12.7}$ sec^{-1}) for (29) can thus be derived from the loss of internal rotations of the vinyl group and the subsequent formation of two planar allyl radicals where each restricts three carbons and four hydrogens to a rigid plane. This compares remarkably well with the pyrolyses of endo- and exo-2-vinylbicyclo[2.2.2]oct-5-ene (20 and 21 respectively). As previously cited, both epimers in all probability undergo transformation to cis-$\Delta^{1,6}$-hexalin (22) through diradical intermediates. In each case, two planar allyl radicals are formed, and an expectedly lower ΔS^* (-3.3 eu) and A factor ($10^{12.8}$ sec^{-1}) result.[13]

In similar fashion, the formation of a pentadienyl radical restricts five carbons and six hydrogens to a single plane, so that the pyrolysis of

1,1-divinylcyclopropane (1) (ΔS^* = -4.1 eu, A = $10^{12.6}$ sec^{-1}, solution phase)[47] and of 1,1-divinyl-3-methylene-cyclobutane (2) (ΔS^* = -6.7 eu, A = $10^{11.9}$ sec^{-1}, solution phase) have expectedly lower values.

In conclusion, characteristically large ΔS^* values were not observed for either the pyrolysis of 1,1-divinyl-3-methylenecyclobutane (2) or methylene-3-vinylcyclobutane (29). It is, therefore, difficult to rationalize any element of concert in these reactions when a diradical pathway can accomodate the data better.

The question also arises as to whether the observed activation energies for the thermal reorganizations of (2) and (29) are compatible with diradical pathways. Comparison of the differences in the activation energies of suitably chosen models of known diradical processes can be employed to estimate the activation energies for the pyrolyses in question. It is noteworthy to point out that since this activation energy estimate is derived from known diradical reactions, it follows that the estimate is also one for a diradical process involving the same type of rate-determining step. Corroboration of the estimate with experimental observation would thus support the concept of a diradical mechanism. For example, a diradical process has been established for the rearrangement of vinylcyclopropane to cyclopentene.[12b] The isomerization of cis-1,2-dideuteriocyclopropane requires about 65 kcal/mol.[43] If full use is made of the allylic delocalization energy

(estimated at 12-21 kcal/mol),[48] the reaction would require at most 53 kcal/mol (65 - 12). Within the uncertainty limits of the allyl delocalization energy, the estimated and observed value (about 50 kcal/mol)[38] are in good agreement. Since other chemical data support the concept of a diradical pathway for this rearrangement, it follows that the total contribution of the allyl group to a reduction in the activation energy amounts here to 15 kcal/mol (65 - 50).

Adapting this above procedure, an activation energy estimate for the pyrolysis of methylene-3-vinylcyclobutane (29) requires a comparison of the isomerization of cis-1,2-dideuteriocyclobutane with the degenerate rearrangement of methylenecyclobutane and also with the ring expansion of vinylcyclobutane. Unfortunately, only the data on the degenerate rearrangement of methylenecyclobutane (E_a = 49.5 kcal/mol) are available.[49] The isomerization of cis-1,2-dimethylcyclobutane requires 61.3 kcal/mol.[50] By their inspection of the data compiled on the thermal unimolecular reactions, Willcott, Cargill, and Sears conclude that each alkyl substituent reduces the activation energy for the isomerization by about 3 kcal/mol,[42] so that as a working model we can infer an activation energy for the isomerization of cis-1,2-dideuteriocyclobutane at 67.3 kcal/mol (61.3 + 3 + 3). Thus, incorporation of an exocyclic double bond into the cyclobutane system imparts 17.8 kcal/mol (67.3 - 49.5) reduction in the activation energy. The thermoreorganization of isopropenylcyclobutane

(E_a = 51.0 kcal/mol) offers the closest analogy to the unknown activation parameters for the pyrolysis of vinylcyclobutane. Comparison of this value with the activation energy estimate of 67.3 kcal/mol for the isomerization of cis-1,2-dideuteriocyclobutane might be used to ascertain the extent of the assistance of the vinyl group in the transition state, determined here at 16.3 kcal/mol (67.3 - 51.0). Combining the contributions from both moieties in the transition state, places the total stabilization assistance at 34.1 kcal/mol (17.8 + 16.3). When this value is subtracted from the estimated activation energy for the parent cis-1,2-dideuteriocyclobutane, an estimate of 33.2 kcal/mol (67.3 - 34.1) results which, when considering the number of assumptions made, is in remarkable agreement with experimental observation (35.7 kcal/mol). Since the models used to arrive at this estimate all involve diradical processes with rate-determining diradical formation, it follows that our experimental finding is in very good accord with a multistep process involving rate-determining ring cleavage.

An estimate for the pyrolysis of 1,1-divinyl-3-methylenecyclobutane (2) also requires a comparison of the isomerization of cis-1,2-dideuteriocyclobutane (E_a at about 67.3 kcal/mol) with the degenerate methylenecyclobutane rearrangement (E_a = 49.5 kcal/mol).[49] However, knowledge of the contribution by a pentadienyl group to the reduction of the activation energy for the thermolysis is necessary.

By subtraction of the activation energy for the isomerization of cis-1,2-dideuteriocyclopropane (E_a = 65.1 kcal/mol)[43] with the activation energy for the thermal rearrangement of 1,1-divinylcyclopropane (1) (E_a = 42.5 kcal/mol),[51] 22.6 kcal/mol assistance results. The two moieties contribute a total therefore of 40.4 kcal/mol (17.8 + 22.6) assistance in lowering the activation energy. Thus, an estimate of 26.9 kcal/mol (67.3 - 40.4) is in excellent agreement with the observed activation energy of 27.3 kcal/mol. Again the estimate was derived from activation energies of known diradical processes, involving rate-determining diradical formation and supports the concept of a multistep process with rate-determining ring cleavage. Moreover, from our data and by comparison with the degenerate methylenecyclobutane rearrangement, and independent estimate for the total contribution of a pentadienyl group in the transition state can be placed at 22.2 kcal/mol (49.5 - 27.3) which lends weight to the heretofore sole determination of this value as ascertained from the pyrolysis of (1).

In order to construct an energy diagram consistent with a diradical pathway, it must be demonstrated that the heat of formation ΔH_f° for the biradical, formed in the thermo-reorganization of either (2) or (29), is sufficiently below the corresponding heat of formation of the transition state $\Delta H_f^{\circ *}$. By employing the group equivalent method, devised by Franklin[52] and most recently modernized by Benson,[37]

the ΔH_f° for methylene-3-vinylcyclobutane (29) has been calculated at 48.7 kcal/mol. The pyrolysis of (29) required a 35.7 kcal/mol activation energy E_a, so that the heat of formation of the rate-determining transition state $\Delta H_f^{\circ *}$ (where $\Delta H_f^{\circ *} = E_a + \Delta H_f^\circ$) is 84.4 kcal/mol. The strength of the bond involved in this homolysis is weakened by its inclusion in the highly strained methylenecyclobutane (E_{strain} = 28.2 kcal/mol)[53] and by the involvement of two resulting allyl resonance-stabilized groups. The strength of this bond can thus be assessed by subtracting out these contributions from the bond dissociation energy BDE of a suitable model. Isopentane may be just such a model in that it is a trialkyl-substituted ethane as is the weakest bond in (29). The BDE for isopentane is quoted at 80 kcal/mol.[37] Since isopentane already includes the effect of substituents in reducing the strength of the C-C bond, one need only employ the allylic delocalization energy ADE (estimated at 12-21 kcal/mol)[48] to correct for the contribution of the allyl groups. Thus, the strength of the bond involved in this homolysis is <u>at most</u> 27.8 kcal/mol (80 - 28.2 - 2 x 12). In other words, the formation of this biradical requires 27.8 kcal/mol more than the ΔH_f° for (29), so that the ΔH_f° for the biradical is <u>at most</u> 76.5 kcal/mol (27.8 + 48.7). An alternative calculation for the ΔH_f° for the $(allyl)_2CH_2$ biradical at 75.8 kcal/mol by the group equivalent method[37, 54] compares favorably with that above. The higher of these two values is still

well below the $\Delta H_f^{\circ *}$ and very consistent with a biradical mechanism for the thermolysis of (29). An energy diagram has thus been constructed in Figure 1.

A heat of formation ΔH_f° for 1,1-divinyl-3-methylene-cyclobutane (2) was evaluated at 67.8 kcal/mol. It follows that the $\Delta H_f^{\circ *}$ is 95.1 kcal/mol (67.8 + 27.3). The strength of the bond involved in this homolysis can be compared to neopentane (BDE = 77 kcal/mol),[37] provided that corrections are made for its inclusion in the highly strained methylenecyclobutane and for the involvement of the resulting allyl and pentadienyl resonance-stabilized groups, both factors which weaken the bond in (2). The ADE has been previously assessed at a minimum value of 12 kcal/mol.[48] From the difference in activation energies of the pyrolysis of (1) (E_a = 42.5 kcal/mol)[51] and the decomposition of 1,1-diethylcyclopropane to 3-ethyl-2-pentene (E_a = 63.4 kcal/mol),[54] an evaluation of the pentadienyl delocalization energy PDE at 20.9 kcal/mol results. Thus, the strength of the bond involved in this homolysis is <u>at most</u> 16.1 kcal/mol (77 - 28.2 - 12 - 20.9), and the ΔH_f° for the allyl-CH_2-pentadienyl biradical is <u>at most</u> 83.9 kcal/mol (16.1 - 67.8). By employing the group equivalent method, ΔH_f° for the allyl-CH_2-pentadienyl biradical was calculated at 89.2 kcal/mol[37, 54] and compares favorably with the alternate value above. The higher of these ΔH_f° estimations for the biradical is still approximately 6 kcal/mol below

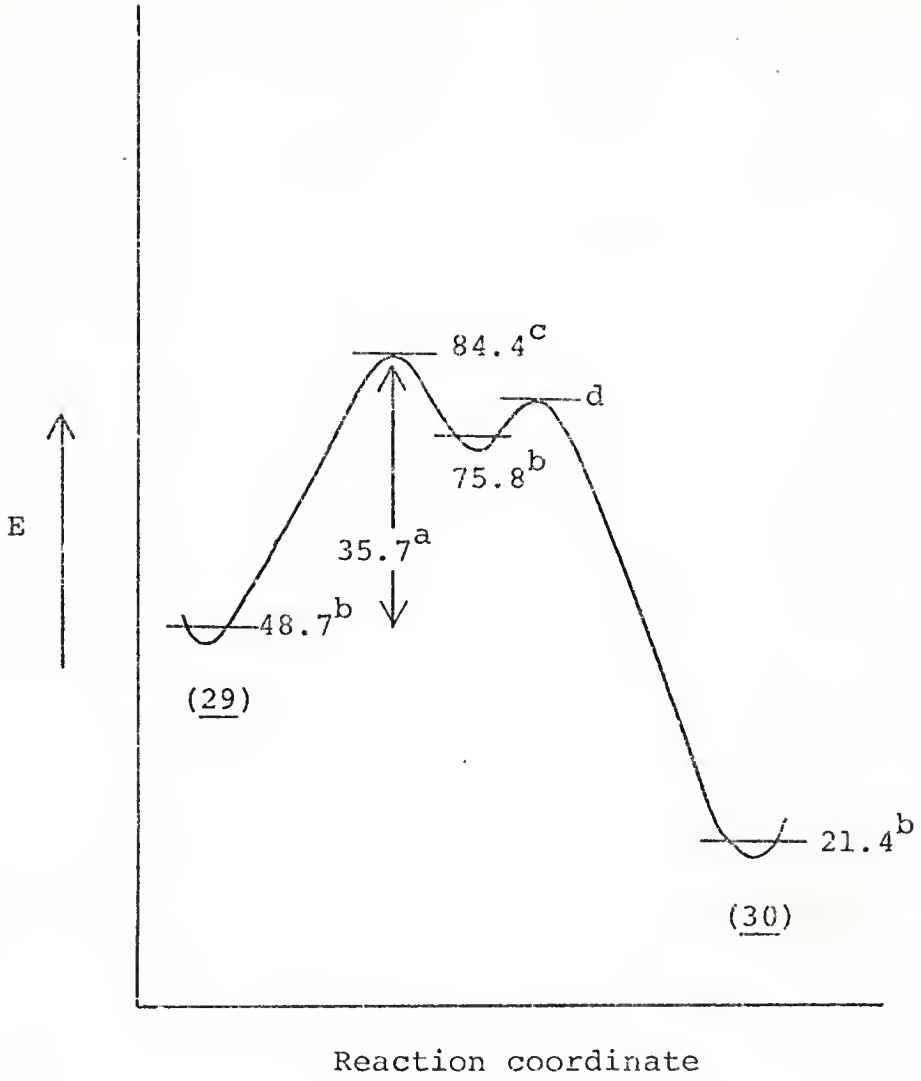
the corresponding $\Delta H_f^{\circ *}$ and is quite consistent only with a biradical pathway for the rearrangement of (2). An appropriate energy diagram for the pyrolysis of (2) has been constructed in Figure 2.

Lastly in an effort to promote further understanding of the mechanism in question here and to emphasize the effectiveness of secondary deuterium isotope effects as a tool for probing the nature of the transition states in thermoreorganizations, a secondary deuterium isotope effect study was accomplished in the thermal transformation of 1,1-divinyl-3-methylenecyclobutane (2).

For contrast recall that an inverse intermolecular secondary deuterium isotope effect ($k_H/k_D = 0.94\pm0.02$) was measured for the Cope reaction of the substituted 1,5-hexadiene (24).[21] As previously stated, with the

(24) or (24-d_2) (25) or (25-d_2)

development of a cyclic multicentered transition state, the sp^2 carbon at C-6 becomes more sp^3-like, so that the steric requirement of H attached at the more congested tetrahedral orientation of the sp^3 position, compelled (24) to rearrange to (25) more reluctantly than (24-d_2) to (25-d_2).



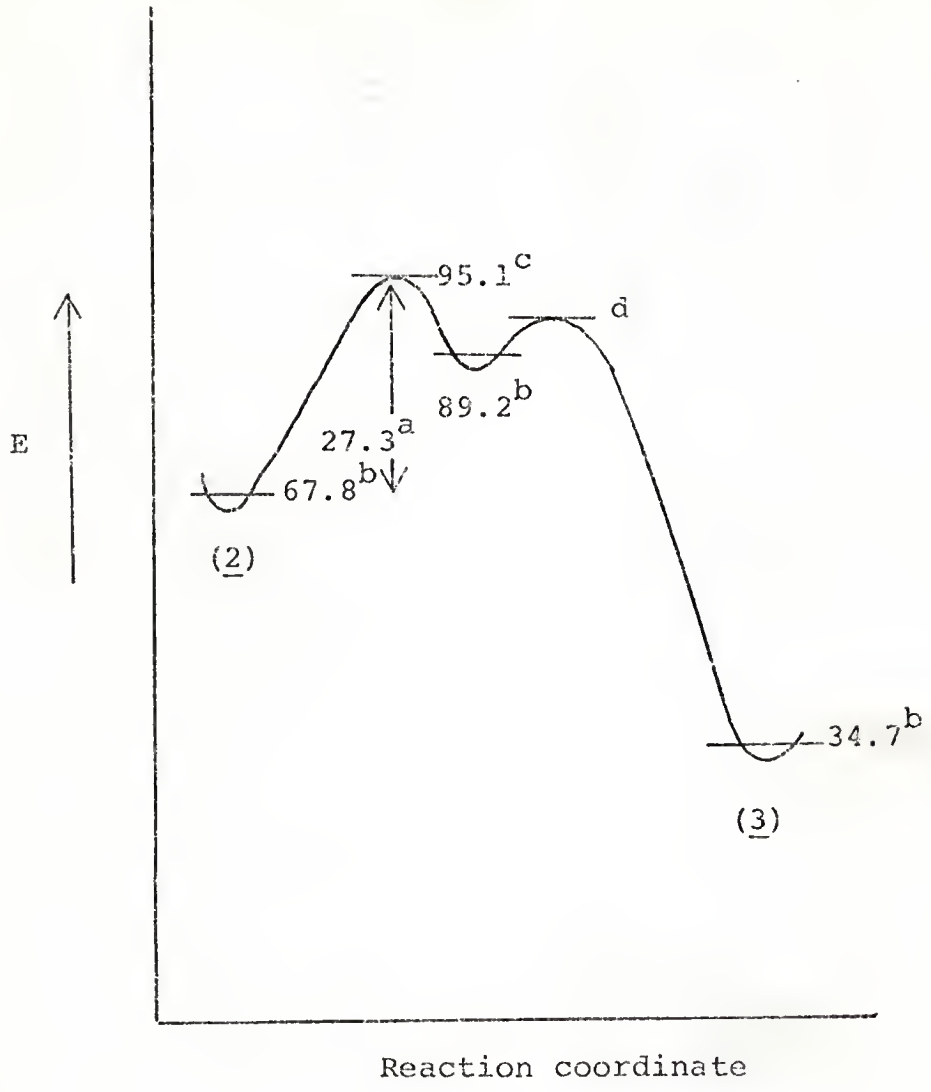
a Observed E_a

b Calculated ΔH_f° by the group equivalent method

c $\Delta H_f^\circ = E_a + \Delta H_f^\circ$

d Speculation

Figure 1: Energy diagram for the pyrolysis of (29)



a Observed E_a

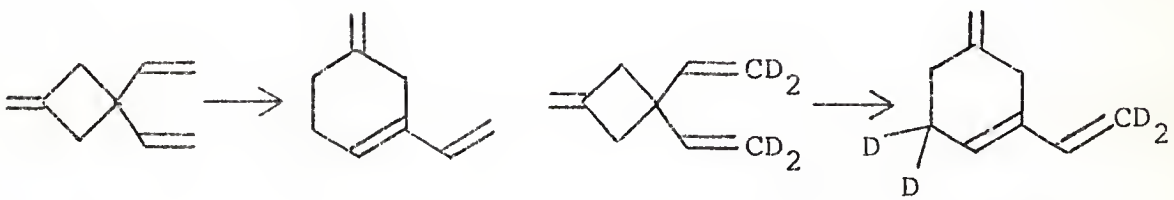
b Calculated ΔH_f° by the group equivalent method

c $\Delta H_f^\circ = E_a + \Delta H_f^\circ$

d Speculation

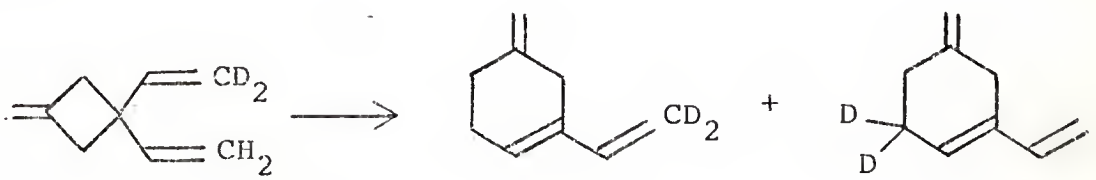
Figure 2: Energy diagram for the pyrolysis of (2)

Observation of normal secondary kinetic deuterium isotope effects in the thermoreorganization of 1,1-divinyl-3-methylenecyclobutane (2) initially prejudiced our inclination to envision the mode for rearrangement as one which involved the intermediacy of diradicals. An intermolecular isotope effect (k_H/k_D = 1.05±0.03) was determined by a competitive rate study of (2) with (2-d_4).



(2) (3) (2-d_4) (3-d_4)

Moreover, a normal intramolecular isotope effect (k_H/k_D = 1.14±0.07) was also observed. It was arrived at by determining the product ratio (3a/3b) in the thermolysis of (2-d_2).

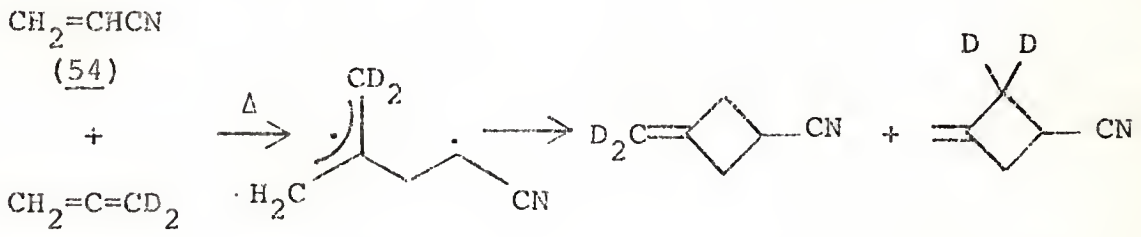


(2-d_2) (3a) (3b)

Insight into the significance of a comparison of inter- and intramolecular isotope effects was first gained in a study of allene cycloadditions. Specifically, Dolbier and Dai examined [2 + 2]-cycloadditions of allene with acrylonitrile (54) and placed it in perspective with other

allene cycloadditions.[56] A comparison of rates of cycloaddition of allene versus allene-d_4 with (54) produced a normal intermolecular isotope effect at 1.04±0.02 and established the nonsynchronous formation of the cycloadduct. Moreover, if both new sigma bonds were formed in a concerted reaction, the intramolecular isotope effect would also be inverse, since in this case the rate-determining step is also product-forming. Employing 1,1-dideuterioallene to introduce isotopic discrimination, enabled them to observe product-forming destruction of the resonance-stabilized allyl radical. The ratio of (55a/55b) of 1.17±0.04 defined the magnitude of the intramolecular isotope effect. The nonidentity of the inter- and intramolecular isotope effects thus indicated that rate-determining and product-forming steps cannot be one and the same, so that a multistep diradical process must be operative. The normal intramolecular isotope effect was initially considered anomalous. For cycliztion there apparently is a small but significant activation energy, the bulk of which the authors ascribed to the rotation of a terminal methylene group from its planar allyl configuration to an orthogonal one. At that time it was thought that the possible source of this normal intramolecular isotope effect might be the relief of nonbonded and torsional interactions which would be found in the planar allyl but not in the nonplanar allyl system. Thus, the unlabelled methylene group would be more apt to rotate to

achieve nonplanarity. More recently, the source of this isotope effect was conceived in a different but supportive light and will be detailed later. To complete the picture,



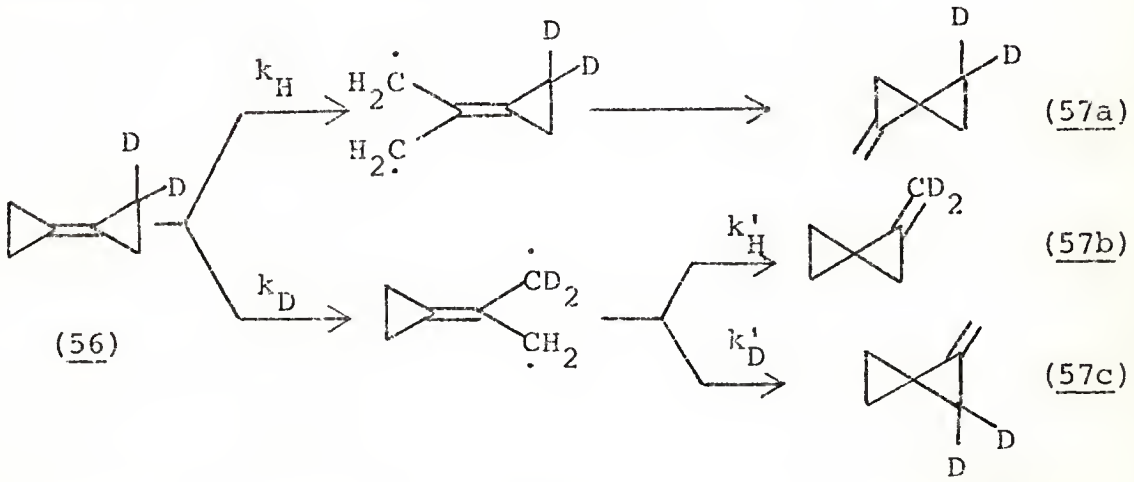
planar (55a) (55b)

[2 + 2]-cycloaddition was complicated by a concomitant degenerate methylenecyclobutane rearrangement.[49] When carried to complete equilibration, a predictably inverse isotope effect (k_H/k_D = 0.92±0.01) was observed and thus was not responsible for the observed kinetic effect.

In dimerizations of parent allene, 1,2-cyclononadiene,[56] and 1,2-cyclohexadiene,[57] normal intramolecular isotope effects were also observed in every case. For the former two dimerizations, normal intermolecular isotope effects were determined and found to be less than the intramolecular isotope effects. Again nonplanar radicals had to be invoked to rationalize the nonidentity of the two isotope effects, and the fact that they are normal.

The utility of a secondary deuterium isotope effect study was additionally demonstrated in the thermal rearrangement of dideuteriobiscyclopropylidene (56) to the deuterated methylenespiropentanes (57a, 57b, and 57c).[26b]

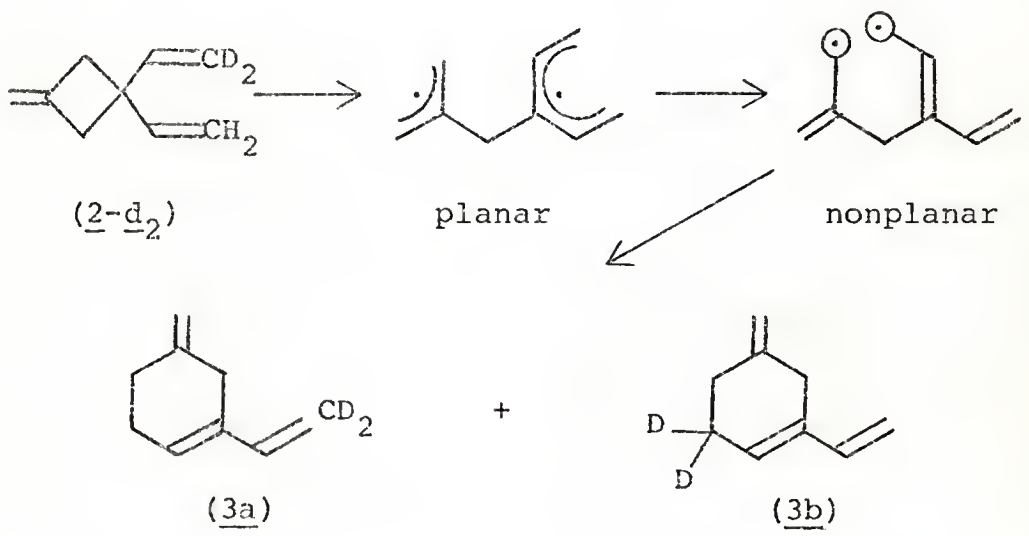
Two distinct isotope effects were operative in this system, defined according to the scheme depicted below, where (57b/57c) = $(k'_H/k'_D)_{cyclization}$ = 1.14±0.02 and where (57a/57b + 57c) = $(k_H/k_D)_{cleavage}$ = 1.24±0.03.



Although one possible concerted or "pivot" type mechanism for this rearrangement cannot be rigorously excluded, the observed isotope effects can be completely rationalized by invoking a diradical pathway. It was believed that the large normal isotope effect for ring cleavage stemmed from the generation of a transition state which is "looser" or "less rigid" than the reactant and where on proceeding to the transition state there is a reduction of the rotational barrier or torsional force constant for the CH_2 twisting motion as the C-C ring bond is weakened. Moreover, the authors point out that the normal isotope effect for cyclization is consistent with the intramolecular isotope effect associated with rotation of a terminal methylene group to form a nonplanar allyl radical followed by simple radical combination to product. The magnitude of this

isotope effect is nearly identical to other intramolecular isotope effects reported for allene cycloadditions.[56]

A normal intramolecular isotope effect (k_H/k_D = 3a/3b = 1.14±0.07) was also observed in the pyrolysis of (2-d_2). The unique feature of this kind of isotope effect



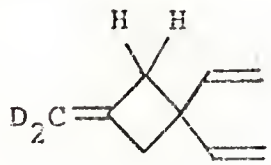
is that it allows one to observe isotopic discrimination after the formation of a planar diradical intermediate. The main energy event in this discrimination is thought to involve a twisting motion of an isotopically substituted, terminal methylene group, resulting in a nonplanar pentadienyl radical with concomitant destruction of π-bonding at its terminus. This twisting implies that there is a drastic lowering of the force constant associated with π-bonding which, in the limiting case, where the CX_2 (X_2 = H_2 or D_2) group twists a full 90°, falls to zero. Conceivably then a single potential energy surface approximates the discrimination process where the CH_2 group,

because of its relatively higher zero point energy, has a head start over the CD_2 group in surmounting this rotational energy barrier. Hence, H preferentially occurs within the cyclohexene ring, and significantly more of (3a) is formed. This recent concept supports an earlier rationalization where relief of nonbonded and torsional interactions, which would be found in the planar but not in the nonplanar conjugated radicals, was used to account for normal intramolecular isotope effects. Despite the large error associated with the intramolecular isotope effect determination, the value is still substantially greater than and different from the normal intermolecular isotope effect. This then is significant. The intramolecular isotope effect must be associated with product formation. Ring cleavage or biradical formation must be associated then with the intermolecular isotope effect, since by definition it is involved solely with the rate-determining step. These conclusions are consistent with the observed activation energy parameters previously examined. Moreover, the mean values for the intermolecular (1.08) and the intramolecular (1.12) isotope effects associated with the 1,1-divinylcyclopropane systems also indicated, albeit narrowly, that the isotope effects may indeed be appreciably different enough from one another. Thus, the same kind of conclusions in the rearrangement of 1,1-divinylcyclopropane (1) to vinylcyclopentene (28) may be drawn.

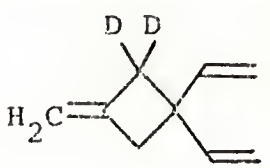
It appears then that the normal intermolecular isotope effect for 1,1-divinyl-3-methylenecyclobutane systems must be derived from a rate-determining ring cleavage step. In that event, there should result a decrease in the torsional force constant or in the rotational barrier for the CX_2 twisting motion as the C-C ring bond weakens. The same explanation was used to rationalize the normal ring cleavage isotope effect in the pyrolysis of dideuteriobiscyclopropylidene (57).[26b] Moreover, biradical formation requires the transformation of the isotopically labelled CX_2 site from sp^2 to sp^2-radical on proceeding toward the transition state. This bears some analogy to Pryor's work on the addition of radicals to styrene where the same kind of transformation occurs in a rate-determining step and where a small but normal intermolecular isotope effect resulted.[27] Thus, both theoretical arguments and experimental analogy support the concept that (2) could in fact undergo rate-determining biradical formation at a faster rate than (2-d_4).

With the knowledge that diradicals intervene in these thermoreorganizations, particularly of (2), where a secondary deuterium isotope effect study conclusively demonstrated the mechanistic pathway for rearrangement, the question arises as to what extent ring closure to product occurs by way of 1,3 versus 3,3 radical combination. To begin to investigate this additional

mechanistic complexity would necessitate an examination of the thermolyses of two novel isotopic isomers (2a) and (2b).



(2a)



(2b)

Two factors complicate an evaluation of the partitioning between these two kinds of ring closure; (a) a competing degenerate methylenecyclobutane type rearrangement,[49] favoring the accumulation of D at the more crowded ring methylene site or (2b), and (b) with the formation of a planar allyl radical, its terminal CH_2 group would rotate out of conjugation preferentially over its CD_2 group in the product-making step. The former factor emphasizes the need to study the thermoreorganizations of both isotopic isomers. Needless to say, the entire evaluation becomes a very complex one and will not be delved into further here.

Systematically evidence for distinguishing the mechanistic mode for the thermoreorganizations of the methylene-3-vinylcyclobutanes (2) and (29) has been presented. Examination of molecular models suggested that concert in these reactions required an unbearably high angle strain for development of cyclic multicentered transition states, as opposed to strain free diradical intermediates. Very low ΔS^* and A factor values characteristic of the Cope reaction were not observed. Instead the low ΔS^* and A factor values could very

reasonably be accounted for by the loss of internal rotations of the vinyl group(s), and the subsequent restriction of a number of atoms to two rigid planar conjugated radicals. Estimations of the activation energy for a diradical process from model systems agreed remarkably well with experimental observations. No evidence of concert was uncovered from a comparison of heat of formation calculations. The heats of formation of the transition state for a diradical process were approximated by the group equivalent method, and these were consistent with the lower heats of formation, calculated for the speculated diradical intermediates. Moreover, the nonidentity of the two secondary deuterium isotope effects for the 1,1-divinyl-3-methylenecyclobutane systems cannot be attributed to a common transition state for the rate-determining and the product-forming steps. In addition, the preponderant weight of analogy indicates that transformation of an isotopically substituted carbon from a trigonal to a tetrahedral orientation should be associated with an inverse secondary deuterium effect. The normal intermolecular and intramolecular deuterium isotope effects can be better accounted for by invoking diradical intermediates. The intramolecular isotope effect has allowed observation of the discrimination process after formation of a planar diradical intermediate and is thus associated with the product-forming step. The intermolecular isotope effect has allowed observation of the

discrimination process in the rate-determining step and must be associated with ring cleavage resulting in biradical formation. Thus, valuable corroborative insight into the nature of the transition states for bond-breaking and bond-making has been gained from the use of secondary deuterium isotope effects as a mechanistic probe.

EXPERIMENTAL

Both boiling and melting points were uncorrected, the latter taken on a Thomas-Hoover melting point apparatus. Infrared spectral data were obtained from either a Perkin-Elmer model 137 or from a Beckman model IR-10 spectrophotometer, and all absorption bands were listed in cm^{-1}. The ultraviolet spectrum was recorded on a Cary model 15 spectrometer. Nuclear magnetic resonance spectra were obtained from a Varian model A-60A unless specified as a XL-100 model. All nmr spectra utilize TMS as an internal standard. Mass spectral data were obtained from an Hitachi Perkin-Elmer RMU-6E spectrometer.

Elemental analyses were determined by Atlantic Microlab, Inc., Atlanta, Georgia.

The glpc analyses and separations were carried out on a Varian Aerograph model A-90P gas chromatograph, equipped with the column listed in the text.

Glpc kinetic analyses were performed on a Hewlett-Packard model 5710A gas chromatograph with flame ionization detector. The chemical composition of the kinetic samples was determined with a Vidar Autolab 6300 digital integrator. First-order, least squares programs were used in conjunction with a pdp 8/e digital computer.

A Lauda constant temperature circulator type N/S15/12, equipped with an R-10 electronic relay, an R-20 electronic controller, and an R-30 temperature and level protection relay, was used for all pyrolyses.

All reagents which are not referenced were commercially available.

Diethylmethylenemalonate (31)

This compound was prepared by a procedure modified after that of Bachman and Tanner.[58] In a typical procedure, a three-necked 2 l. flask, fitted with an overhead stirrer, a thermometer, and a West condenser, was charged with 400 g (2.50 mol) of diethylmalonate, 150 g (5.00 mol) of paraformaldehyde, 25 g of $Cu(OAc)_2$, 25 g of KOAc, and 1000 g of HOAc. The contents were heated at reflux for 60 min. Immediately after reflux, the condenser was readjusted and adapted for distillation at atmospheric pressure in which all the HOAc was distilled in about 2 hr. The remainder was cooled at once, treated with an equal volume of water, and extracted with 2 l. of ether. The ether extract was washed well with water and dried over Na_2SO_4 overnight. After removal of ether by rotary evaporation, the product was distilled at ca. 105-130°/10 mm (lit.[58] 210°/760 mm), yielding 124 g (29% based on the amount of diethylmalonate used). Nmr (CCl_4): δ 1.28 (t, 6H, J = 7 Hz), 4.22 (q, 4H, J = 7 Hz), 6.37 (s, 2H).

Diethyl-3-methylene-1,1-cyclobutanedicarboxylate (32)

A 1.4 l. stainless steel rocker bomb was charged with 353 g (2.05 mol) of diethylmethylenemalonate (31), 41 g (1.03 mol) of allene, 150 ml of toluene, and 2 g of hydroquinone. The bomb was heated to 220° for 18 hr with agitation and under autogenous pressure. After cooling to room temperature, the bomb was opened and the contents distilled at 148-153°/53 mm, yielding 120 g (55%). Ir (neat, NaCl): 3000, 2950, 1735, 1690, 1270, 1180, 1100, 1020, 890; nmr (CCl_4): δ 1.21 (t, 6H, J = 7 Hz), 3.15 (t, 4H, J = 2.5 Hz), 4.17 (q, 4H, J = 7 Hz), 4.81 (p, 2H, J = 2.5 Hz); mass spectrum: m/e 212 (M^+).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.22; H, 7.64. Found: C, 62.19; H, 7.57.

3-Methylene-1,1-cyclobutanedimethanol (33)

In a three-necked 5 l. flask, a solution of 106.0 g (0.500 mol) of diester (32) in 700 ml of dry ether was added dropwise over a 6-hr period to a well-stirred slurry of 47.5 g (1.25 mol) of $LiAlH_4$ in 2800 ml of dry ether. After addition, the pot contents were refluxed for 3 hr, followed by hydrolysis with 48 ml of water, 48 ml of 15% NaOH, and 48 ml of water. The white lithium salts were subjected to Soxhlet extraction with refluxing ether for 48 hr. The combined ether portions were dried over Na_2SO_4 overnight giving 47.6 (75%) yield. Bp: 91-93°/0.30 mm; ir (neat, NaCl): 3380, 2900, 1670, 1030, 880; nmr (CCl_4): δ 2.41 (t, 4H, J = 2.5 Hz), 3.65 (s, 4H), 3.90 (s, 2H),

4.79 (p, 2H, J = 2.5 Hz); mass spectrum: m/e 128 (M^+).

3-Methylene-1,1-cyclobutanedimethanol-di-p-toluenesulfonate (34)

In a three-necked 1 l. flask, 50 g (0.392 mol) of (33) in 155 g (1.96 mol) of dry pyridine[59] was well stirred and cooled to ca. -10° with an ice-salt bath. To this in small portions over a 3-hr period, 186.4 g (0.980 mol) of finely powdered p-toluenesulfonylchloride was added through a solid addition funnel. The system was continuously subjected to a dry argon flow throughout the reaction, and the pot temperature was always maintained below 5°. After addition of the tosylchloride was complete, the reaction mixture was stirred at below 0° for 90 min more and then warming to 25° for only 30 min. The pasty material that resulted was poured into a vigorously stirred mixture of cracked ice and water and stirred, until all the ice had melted and the paste solidified. The solid was filtered from the ice water, recrystallized from absolute ethanol, and dried over full vacuum. A total of 145 g (85%) of a white powdery solid was obtained. Mp: 108-110°; ir (KBr): 3070, 2970, 1600, 1380, 1180, 1150, 970, 900, 835, 315; nmr ($CDCl_3$): δ 2.35-2.54 (m, 10H), 4.04 (s, 4H), 4.85 (p, 2H, J = 2.5 Hz), 7.54 (AB q, 8H); mass spectrum: m/e 436 (M^+).

1,1-Bis(bromomethyl)-3-methylenecyclobutane (35)

In a three-necked 5 l. flask, 70.0 g (0.160 mol) of (34) in ca. 4000 ml of acetone, dried by distillation over

molecular sieves 4A, K_2CO_3, and $KMnO_4$, was well stirred. To this in one portion, 97.2 g (1.12 mol) of anhydrous LiBr was added, and the pot contents were heated to reflux for 20 hr. After reflux, the acetone was removed by rotary evaporator, and the residual liquid was taken up in ether. The ether solution was washed well with water and a saturated NaCl solution, and it was then dried overnight over Na_2SO_4. The product was purified by fractional distillation at 54-55°/0.75 mm giving 32.2 g (79%) of a colorless liquid. Ir (neat, NaCl): 2940, 1675, 1420, 1238, 889; nmr (CCl_4): δ 2.63 (t, 4H, J = 2.5 Hz), 3.68 (s, 4H), 4.95 (p, 2H, J = 2.5 Hz); mass spectrum: m/e 254 (M^+), 256 ($M^+ + 2$), 256 ($M^+ + 4$).

3-Methylene-1,1-cyclobutanediacetonitrile (36)

In a three-necked 1 l. flask, fitted with an overhead stirrer, a Friedrich condenser with a $CaCl_2$ drying tube, a thermometer, and a pressure-equalizing dropping funnel, 76.8 g (1.18 mol) of KCN in 100 ml of dry DMSO was heated to 70-80°, and to this a solution of 30.0 g (1.18 mol) of (35) in 100 ml of dry DMSO was added dropwise over a 3-hr period. During the addition the temperature was maintained between 75-85°, and, after the addition was complete, the reaction mixture was heated to 80-90° for 42 hr. The cooled pot contents were diluted with 800 ml of water. The aqueous DMSO solution was extracted with ca. 3 l. of ether. The ether solution was then washed with water to remove any last traces of DMSO and dried overnight over

Na_2SO_4. The product was purified by fractional distillation at 93-94°/0.25 mm, yielding 15.0 g (87%) of a colorless liquid. Ir (neat, NaCl): 2910, 2250, 1675, 1415, 890; nmr (CCl_4): δ 2.70 (s, 4H), 2.74 (t, 4H, J = 2.5 Hz), 4.99 (p, 2H, J = 2.5 Hz); mass spectrum: m/e 146 (M^+).

3-Methylene-1,1-cyclobutanediacetic acid (37)

In a one-necked 2 l. flask, 111.6 g of 87% KOH was dissolved in 1200 ml of 50% ethanol. To this, 28.0 g (0.192 mol) of (36) was added in one portion, and the solution was then heated to reflux for 16 hr. The aqueous ethanol was removed completely by rotary evaporator, and the residual solid was redissolved in 150 ml, cooled to 0°, and hydrolyzed with conc. HCl to a pH ≈ 1. The product was extracted with 1200 ml of ether and dried overnight over Na_2SO_4. The product, once freed from ether, could be recrystallized from hot CCl_4 giving 34.0 g (96%) of a white powdery solid. Mp: 122-123°; ir (KBr): 3100, 2900, 2750, 1700, 1650, 1420, 1400, 1340, 1250, 1040, 960, 880; nmr (CD_3COCD_3): δ 2.68 (t, 4H, J = 2.5 Hz), 2.72 (s, 4H), 4.80 (p, 2H, J = 2.5 Hz), 8.79 (s, 2H); mass spectrum: m/e 184 (M^+).

Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.58; H, 6.66.

3-Methylene-1,1-cyclobutanediethanol (38)

The diacetic acid (37) above was reduced by the standard method using $LiAlH_4$ in 72% yield.

Bp: 107.5-110.5°/0.15 mm; ir (neat, NaCl): 3300, 2900, 1670, 1090, 1020, 875; nmr (CCl_4): δ 1.80 (t, 4H, J = 6.5 Hz), 2.45 (t, 4H, J= 2.5 Hz), 3.65 (t, 4H, J = 6.5 Hz), 4.08 (s, 2H), 4.78 (p, 2H, J = 2.5 Hz).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: 68.99; H, 10.29.

3-Methylene-1,1-cyclobutanediethanol-di-p-toluenesulfonate (39)

In a three-necked 50 ml flask, a solution of 4.0 g (0.0256 mol) of (38) in 10.0 g (1.28 mol) of dry pyridine[59] was stirred by magnetic stirring bar and cooled to -10° with an ice-salt bath under a constant dry nitrogen purge. To this 12.2 g (0.0642 mol) of p-toluenesulfonylchloride was added in small portions over a 35-min period. After addition, the contents were allowed to stir for an additional 90 min at -10° to 0° and then allowed to warm to room temperature (taking ca. 20 min). The pot contents were poured over ca. 400 ml of cracked ice and water and vigorously stirred with an overhead stirrer, until all the ice had melted. A peach-colored paste resulted which could be recrystallized from warm methanol. A white crystalline solid was obtained and after drying under full vacuum weighed 10.0 g (84%). Mp: 66-67°; ir (KBr): 2980, 2870, 1665, 1600, 1350, 1180, 1170, 1090, 960, 930, 885, 815, 765; nmr (CCl_4): δ 1.83 (t, 4H, J = 6.5 Hz), 2.40 (t, 4 H, J = 2.5 Hz), 2.48 (s, 6H), 3.95 (t, 4H, J = 6.5 Hz), 4.71 (p, 2H, J = 2.5 Hz), 7.54 (AB q, 8H).

Anal. Calcd for $C_{23}H_{28}O_6S_2$: C, 59.46; H, 6.08; S, 13.80. Found: C, 59.34; H, 6.10; S, 13.80.

1,1-Divinyl-3-methylenecyclobutane (2)

A three-necked 250 ml flask was fitted with a pressure-equalizing dropping funnel, a magnetic stirring bar, and a bent tube connected to two coiled traps in series through which a vacuum pump was connected. The flask was charged with 3.5 g (0.035 mol) of potassium-t-butoxide. To this, a solution of 4.0 g (0.0086 mol) of (39) in 75 ml of freshly dried DMSO[60] was added dropwise over a 45-min period under 0.25 mm vacuum and with the coiled traps, cooled by liquid nitrogen. The reaction temperature was maintained under vigorous stirring at 0.25 mm vacuum for 12 hr more. The volatile compounds were degassed and transferred to a small tube via vacuum line and sealed until purification could be accomplished by gas chromatography on a 5' (18%) DC-200 column at 55°. Two pure products were obtained; 0.21 g (20%) of the desired (2) and 0.10 g (10%) of what was suspected as the isomerized 3,3-divinyl-1-methylcyclobutene. For (2), ir (gas, NaCl): 3045, 2995, 2960, 1680, 1640, 1415, 1220, 994, 915, 880; nmr (100 MHz, $CDCl_3$): δ 2.75 (t, $4H_a$, J_{ab} = 2.7 Hz), 4.82 (p, $2H_b$, J = 2.7 Hz), and an ABX pattern at 5.01 ($2H_c$, J_{cd} = 1.4 Hz, J_{ce} = 16.6 Hz), 5.06 ($2H_d$, J_{cd} = 1.4 Hz, J_{de} = 10.2 Hz), and 6.03 ($2H_e$, J_{ce} = 16.6 Hz, J_{de} = 10.2 Hz); mass spectrum: m/e 121 (9.5), 120 (83.2), 119 (14.6),

117 (8.0), 106 (10.9), 105 (100), 104 (6.9), 103 (14.6), 93 (16.1), 92 (62.8), 91 (93.4), 80 (11.7), 79 (99.3), 78 (25.5), 77 (54.7), 65 (21.9), 63 (11.7), 53 (20.4), 52 (14.6), 51 (27.0), 50 (9.5), 41 (30.7), 40 (20.4), 39 (49.7).

Anal. Calcd for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.87; H, 10.10.

For the suspected 3,3-divinyl-1-methylcyclobutene, ir (gas, NaCl): 3050, 2930, 2900, 2850, 1640, 1480, 1400, 1260, 990, 910; nmr (CCl_4): δ 1.68-1.88 (m, 3H), 2.30-2.50 (m, 2H), 4.72-5.16 (m, 4H), 5.72-6.25 (m, 3H).

4-Methylene-2-vinylcyclohexene (3)

A sealed tube containing a dilute solution of (2) in benzene was heated to 115° for 7 hr giving a nearly quantitative conversion to (3). The product was purified by gas chromatography on a 5' (18%) DC-200 column at 80°. Ir (CCl_4, KBr liquid cell): 3090, 3070, 3000, 2980, 2960, 2910, 2835, 1650, 1638, 1605, 1430, 1335, 1220, 975, 890, 840; nmr ($CDCl_3$): δ 2.30 (s, $4H_a$), 2.85 (s, $2H_b$), 4.55-5.20 (m, $2H_c$ + $2H_d$), 5.52-5.85 (m, $1H_e$), 6.28 (AB q, $1H_f$, J_{trans} = 17 Hz, J_{cis} = 10 Hz); uv (n-decane): λ_{max} 230 nm (ε 22,200), 225 nm (ε 21,300), 238 nm (ε 13,700); mass spectrum: m/e 121 (9.6), 120 (84.3), 119 (14.5), 106 (12.1), 105 (100), 104 (7.2), 103 (15.7), 93 (14.5), 92 (62.7), 91 (91.6), 80 (12.1), 79 (38.6), 78 (22.9), 77 (43.4), 66 (14.6), 65 (20.5), 63 (14.5), 53 (19.3),

52 (13.3), 51 (9.5), 50 (12.0), 41 (43.4), 40 (9.6), 39 (47.0).

Anal. Calcd for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 90.10; H, 9.86.

Kinetic analysis for 1,1-divinyl-3-methylenecyclobutane (2)

A solution of ca. 5% of 1,1-divinyl-3-methylenecyclobutane (2) and ca. 5% of high purity n-nonane (as an internal standard) in ca. 90% of high purity n-decane[61] was prepared in a 30 ml tube. From this homogeneous solution, 25 µl aliquots were withdrawn and transferred by syringe to 6" capillary tubes (O. D. = 7 mm; bore, 1.0-1.5 mm). The capillary tubes were sealed under vacuum with the contents cooled by liquid nitrogen prior to evacuation. In this manner, seventy samples were readied for kinetic runs. Each capillary tube, prior to immersion in hot oil, was protected by a well-fitting wire gauze sleeve. The tubes were heated in a well-insulated and well-stirred oil bath, a Lauda constant temperature circulator type N/S15/12, equipped with an R-10 electronic relay, an R-20 electronic controller, and a R-30 temperature and level protection relay, and filled with Ultra-Therm 330S silicone fluid. Temperatures were monitored both by an NBS thermometer, calibrated in 0.1°, and by using a calibrated chromel-alumel thermocouple in conjunction with a Honeywell model 2702 potentiometer. As few as six, but as many as twelve prepared tubes were

used per temperature run. Each tube was withdrawn from the oil bath at an appropriate time, cooled immediately by a dry ice-isopropanol bath, opened, and analyzed by gas chromatography on a 7.5' (2%) DC-200 column at 56°. The kinetic analyses were performed on a Hewlett-Packard model 5710A gas chromatograph with a flame ionization detector. The chemical compositon of the kinetic samples was determined with a Vidar Autolab 6300 digital integrator by following the disappearance of (2) with respect to the internal standard, n-nonane (see Appendix I). A first-order, least squares program[62] was used in conjunction with a pdp 8/e digital computer to analyze all the data. Rate constants at seven different temperatures were determined and compiled in Table 1.

Table 1

Kinetics for the thermal rearrangement of (2) to (3)

Temp (°C)	Temp (°K)	10^{-3}/Temp (°K)	k x 10^{5} sec
86.1	359.25	2.7836	1.93±0.04
93.2	366.35	2.7296	4.09±0.06
99.9	373.05	2.6806	7.56±0.09
100.7	373.85	2.6749	8.36±0.16
107.1	380.25	2.6298	16.5 ±0.2
114.6	387.75	2.5790	30.9 ±0.5
121.1	394.25	2.5365	57.8 ±0.5

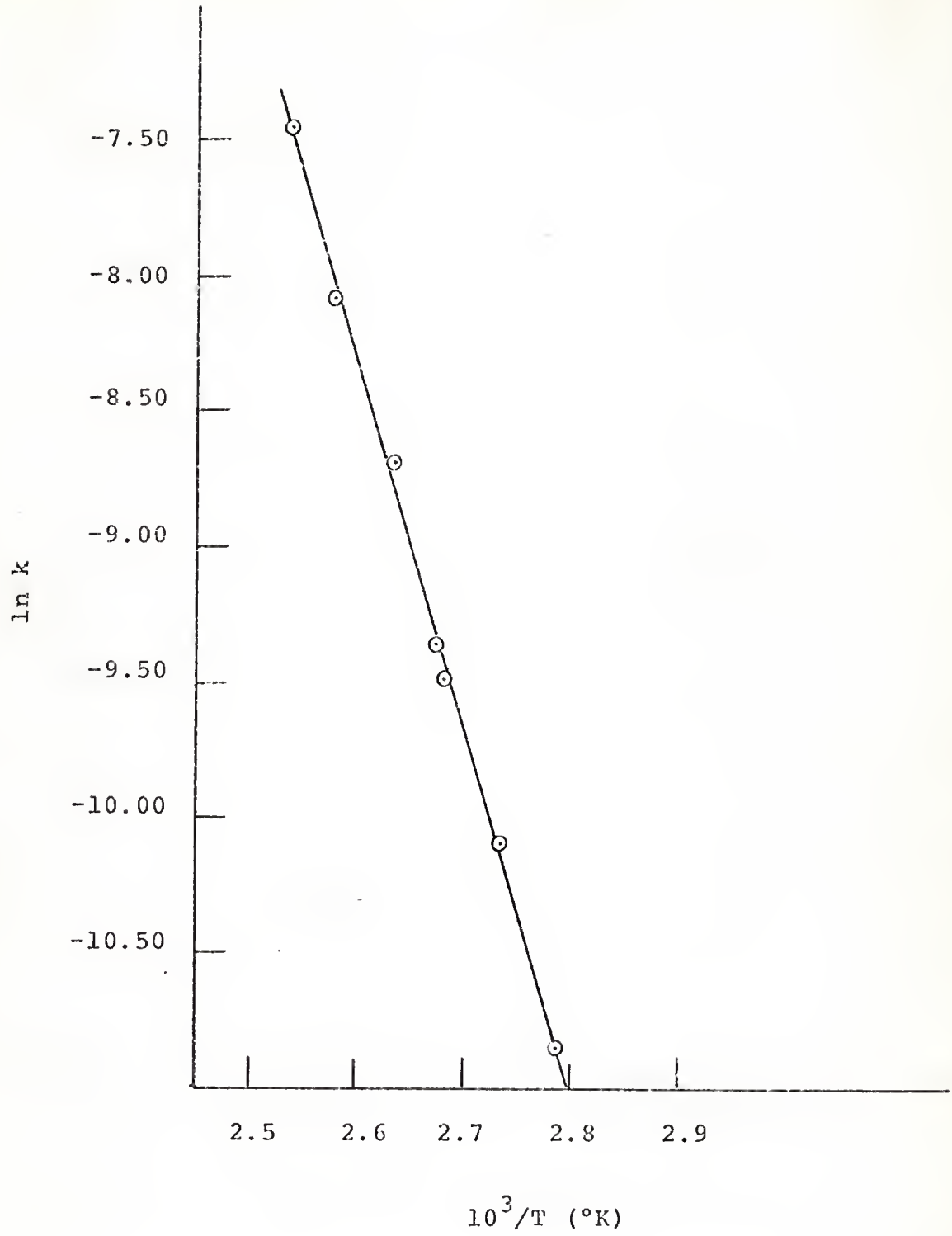


Figure 3: Arrhenius plot for the conversion of (2) to (3).

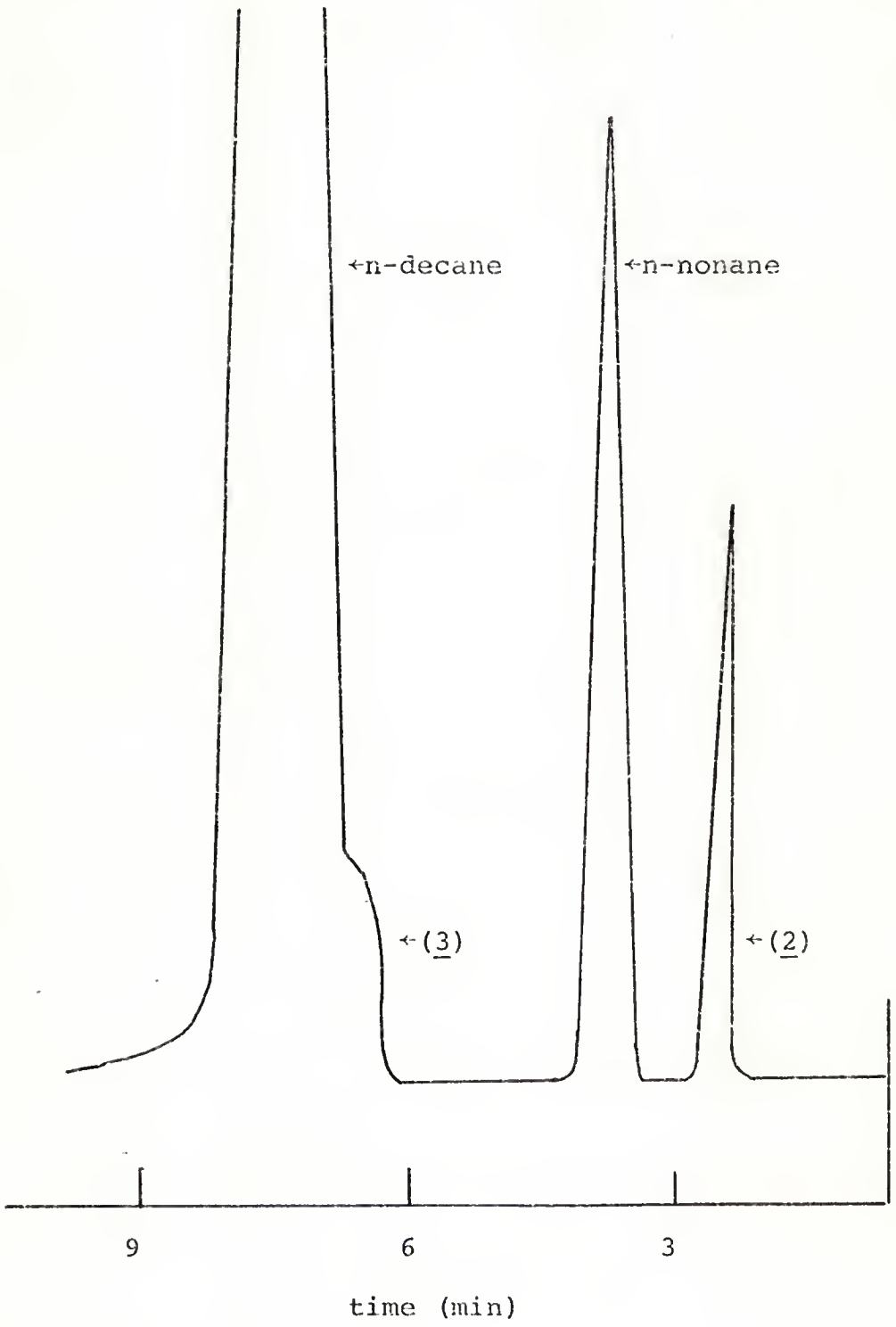


Figure 4: Sample glpc trace of the kinetic analysis for the thermal conversion of (2) to (3)

A computer program was formulated to produce an Arrhenius plot of log k = log A - E_a/RT for this first-order reaction,[62] and it also calculated the appropriate parameters. An Arrhenius plot for these data appears in Figure 3. Energy of activation, 27.27±0.30 kcal/mol; log A, 11.87±0.17; enthalpy of activation, 26.53±0.30 kcal/mol at 103.2°; entropy of activation, -6.66±0.78 cal/mol-deg at 103.2°; free energy of activation, 29.03±0.78 kcal/mol at 103.2°. The correlation coefficient was 0.9997.

3-Methylene-1,1-cyclobutanedi(ethan-α,α-d_2-ol) (38-d_4)

The method used for the reduction of 3-methylene-1,1-diacetic acid (37) in the preparation of (38) was similarly followed by using $LiAlD_4$ in the preparation of (38-d_4) in 68% yield. Bp: 130-131°/0.75 mm; ir (neat, NaCl): 3240, 3030, 2860, 2800, 2180, 2070, 1660, 965; nmr ($CDCl_3$): δ 1.78 (s, 4H), 2.42 (t, 4H, J = 2.5 Hz), 3.83 (s, 2H), 4.78 (p, 2H, J = 2.5 Hz).

3-Methylene-1,1-cyclobutanedi(ethan-α,α-d_2-ol)-di-p-toluenesulfonate (39-d_4)

The procedure used in the bistosylation of (38) was similarly followed with (38-d_4) resulting in a 77% yield. Mp: 67.5-68.5° (methanol); ir (KBr): 3000, 2880, 2230, 2120, 1660, 1350, 965, 890; nmr ($CDCl_3$): δ 1.78 (s, 4H), 2.39 (t, 4H, J = 2.5 Hz), 2.44 (s, 6H), 4.73 (p, 2H, J = 2.5 Hz), 7.52 (AB q, 8H).

Anal. Calcd for $C_{23}H_{24}D_4O_6S_2$: C, 58.95; H + D, 5.16 + 1.72 = 6.88; S, 13.68. Found: C, 58.98; H + D, 6.87; S, 13.61.

3-Methylene-1,1-di(vinyl-2,2-d_2)cyclobutane (2-d_4)

The preparation of this compound was similar to that for (2). Gas chromatography on a 5' (18%) DC-200 column at 55° afforded two hydrocarbons; 0.32 g (17%) of (2-d_4), and 0.21 g (10%) of what was suspected as 1-methyl-3,3-di(vinyl-2,2-d_2)cyclobutene. For (2-d_4), ir (gas, NaCl): 3090, 3010, 2970, 2935, 2320 (w), 2230 (w), 1680, 1600, 1420, 1035, 945, 880, 735; nmr (CCl_4): δ 2.72 (t, $4H_a$, J_{ab} = 2.5 Hz), 4.89 (p, $2H_b$, J_{ab} = 2.5 Hz), 5.85-6.10 (m, 2H); mass spectrum: m/e 124 (M^+).

Anal. Calcd for $C_9H_8D_4$: C, 87.02; H + D, 6.49 + 6.49 = 12.98. Found: C, 86.85; H + D, 12.93.

For the suspected 1-methyl-3,3-di(vinyl-2,2-d_2)-cyclobutene, ir (CCl_4, KBr liquid cell): 2900, 2860, 2320 (w), 2210 (w), 1640, 1580, 1430, 930, 860; nmr (CCl_4): δ 1.70 (q, 3H, J = 1.5 Hz), 2.31 (q, 2H, J = 1.5 Hz), 5.77 (q, 3H, J = 1.5 Hz), 5.90 (m, 2H).

4-Methylene-2-(vinyl-2,2-d_2)cyclohexene-6,6-d_2 (3-d_4)

Into four 1 ml tubes, 400 µl each of ca. 10% (2-d_4) in benzene was transferred by syringe and sealed under vacuum. A protective wire gauze sleeve was placed around each tube, and the contents of the tube were subsequently heated at 120° for 5 hr. Purification was accomplished by gas

chromatography on a 5' (18%) DC-200 column at 60°. The reaction appeared to be quantitative. Ir (CCl_4, KBr liquid cell): 3080, 2990, 2930, 2860, 2190 (w), 2160 (w), 2100 (w), 1680, 1650, 1445, 1070, 1030, 945, 890, 718; nmr (CCl_4): δ 2.26 (s, $2H_a$), 2.82 (s, $2H_b$), 4.67-4.86 (m, $2H_c$), 5.71 ($1H_e$), 6.15-6.36 (m, $1H_f$); mass spectrum: m/e 124 (M^+).

Anal. Calcd for $C_9H_8D_4$: C, 87.02; H + D, 6.49 + 6.49 = 12.98. Found: C, 87.08; H + D, 12.91.

Kinetic analysis for 3-methylene-1,1-di(vinyl-2,2-d_2)-cyclobutane (2-d_4)

A solution of ca. 5% of 3-methylene-1,1-di(vinyl-2,2-d_2)cyclobutane (2-d_4) and ca. 5% of high purity n-nonane (as an internal standard) in ca. 90% of n-decane[61] was prepared in a 10 ml tube. From this homogeneous solution, 25 µl aliquots were extracted and transferred by syringe to 6" capillary tubes. In every remaining detail, the kinetics and their analyses were identical to that already described for (2). The run at each temperature was done immediately following the kinetic run of the respective (2), so that an accurate comparison of rate data of (2-d_4) with (2) could be made with a minimum of error. A first-order, least squares treatment was used in conjunction with a pdp 8/e digital computer to analyze the data. Rate constants were determined at two different temperatures (see also Appendix I) and compiled in Table 2.

Table 2

Kinetics for the thermal rearrangement of (2-d_4) to (3-d_4)

Temp (°C)	Temp (°K)	10^{-3}/Temp (°K)	k x 10^5 sec
99.9	373.05	2.6806	7.17±0.08
121.1	394.25	2.5365	55.4 ±0.8

3-Methylene-1,1-cyclobutanediacetic anhydride (40)

In a 100 ml one-necked flask, 10.0 g (0.0473 mol) of 3-methylene-1,1-cyclobutanediacetic acid (37) was dissolved in 12.0 g (0.118 mol) of acetic anhydride and gently refluxed for 15 min. The pot contents were cooled and subjected to full vacuum for 12 hr. The residual material was recrystallized from a 4:1 solution of pet ether (30-80°) and benzene, collecting 7.8 g (100%). In this manner, more anhydride was made on the same scale until sufficient amounts of product were obtained. Mp: 55-56°; ir (KBr): 2850, 1810, 1760, 1665, 1400, 1150, 950, 890, 810; nmr (CCl_4): δ 2.63 (t, 4H, J = 2.5 Hz), 2.83 (s, 4H), 4.88 (p, 2H, J = 2.5 Hz); mass spectrum: m/e 166 (M^+).

Ethyl, hydrogen-3-methylene-1,1-cyclobutanediacetate (41)

In a 50 ml one-necked flask, 16.0 g (0.096 mol) of (40) was dissolved and heated with 6.8 g (0.150 mol) of absolute ethanol over a steam bath for 2 hr. The excess ethanol was removed by rotary evaporator, and the product distilled at

130-132°/0.45 mm, affording 17.6 g (88%) of a colorless liquid. Ir (neat, NaCl): 3350, 3130, 2900, 1800, 1720, 1650, 1170, 1050, 965; nmr (CCl_4): δ 1.25 (t, 3H, J = 2.5 Hz), 2.50-2.80 (m, 8H), 4.09 (q, 2H, J = 7 Hz), 4.75 (p, 2H, J = 2.5 Hz), 11.05 (s, 1H); mass spectrum: m/e 212 (M^+).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.11; H, 7.59.

1-Acetic acid, 1-ethanol-3-methylenecyclobutane (42)

A total of 39.4 g (0.186 mol) of (41) was divided up into six portions. In a typical run, 6.0 g (0.0351 mol) of (41) along with 5.5 g (0.120 mol) of absolute ethanol were dissolved in liquid NH_3. A dry ice condenser and a dewar, cooled with dry ice and isopropanol were used to maintain NH_3 as a liquid in a 1 l. three-necked flask. Precautions were taken to minimize the condensation of water within the reaction flask. To this cold solution, 2.4 g (0.105 g-atom) of Na was added in small portions at a rate which insured that there was no remaining blue color with each subsequent addition of a Na sliver. After the Na addition was complete, a small amount of absolute ethanol was added to hasten the quenching of the blue color. The liquid NH_3 was allowed to evaporate overnight. The residual material was dissolved in water, cooled to 0°, and acidified with conc. HCl to a pH = 1, followed by ether extraction. The ether extracts were dried over $MgSO_4$ overnight.

After rotary evaporation, the residual liquid was dried over full vacuum for 12 hr. The crude yield weighed 2.9 g (49%) and was used as is in the next step. Ir (neat, NaCl): 3500, 3200, 2980, 2900, 2650, 1760, 1670, 1420, 1300, 1260, 1230, 1070, 885; nmr (CCl_4): δ 1.92 (t, 2H, J = 6 Hz), 2.44-2.76 (m, 7H), 4.26 (t, 2H, J = 6 Hz), 4.82 (p, 2H, J = 2.5 Hz), 7.98 (s, 1H).

3-Methylene-1,1-cyclobutanediethanol-α,α-d_2 (38-d_2)

In a three-necked 2 l. flask, prepurged with dry argon, 4.80 g (0.126 mol) of $LiAlD_4$ was well stirred in 600 ml of freshly dried ethyl ether. To this over 170 min, a solution of 17.2 g (0.115 mol) of crude (42) in 500 ml of freshly dried ethyl ether was added dropwise. After addition, the pot contents were gently refluxed for 4 hr. The pot contents were cooled and hydrolyzed in the usual manner, filtered, and dried over $MgSO_4$. The solid lithium salts were subjected to Soxhlet extraction with refluxing ether and also dried. The product distilled at 113-122°/ 0.30 mm, affording 5.3 g. Ir (neat, NaCl): 3250, 2870, 2800, 2190, 2080, 1670, 1040, 970, 875; nmr ($CDCl_3$): δ 1.55-2.05 (m, 4H), 2.44 (t, 4H, J = 2.5 Hz), 3.64 (t, 2H, J = 8 Hz), 3.87 (s, 1H), 3.98 (s, 1H), 4.78 (p, 2H, J = 2.5 Hz).

3-Methylene-1,1-cyclobutanediethanol-α,α-d_2-di-p-toluenesulfonate (39-d_2)

The procedure used in the bistosylation of (38) was

similarly followed with (38-d_2). Mp: 66-67° (methanol); ir (KBr): 3000, 2890, 2240, 2180, 1900, 1660, 1590, 1345, 1190, 1170, 1095, 960, 935, 875, 870, 765, 708; nmr ($CDCl_3$): δ 1.50-1.96 (m, 4H), 2.20-2.62 (m, 10H), 4.02 (t, 2H, J = 7 Hz), 4.74 (p, 2H, J = 2.5 Hz), 7.55 (AB q, 8H).

Anal. Calcd for $C_{23}H_{26}D_2O_6S_2$: C, 59.20; H + D, 5.62 + 0.86 = 6.48; S, 13.74. Found: C, 59.03; H + D, 6.40; S, 13.65.

3-Methylene-1-vinyl-1-(vinyl-2,2-d_2)cyclobutane (2-d_2)

The preparation of this compound was similar to that for (2). Ir (gas, NaCl): 3090, 3010, 2975, 2940, 2280 (w), 2130 (w), 1680, 920, 880; nmr (C_6D_6): δ 2.87 (t, 4H, J = 2.5 Hz), 4.82-5.18 (m, 3H), 5.21-5.38 (m, 1H), 5.92-6.12 (m, 2H). The exact nmr integration ratio (from a minimum of 10 integrations) of all vinyl H to all allyl H of 1.47±0.01 (should be 1.50), and the exact nmr integration ratio (from a minimum of 10 integrations) of all terminal-vinyl H to all internal-vinyl H of 1.95±0.02 (should be 2.00) both indicate that contaminants (2-d_3) and (2-d_4) may be present. By low voltage (6 ev) mass spectral analysis in the parent peak region, an accurate assessment of the distribution of isotopic isomers was determined: (2-d_2), 0.861; (2-d_3), 0.050; (2-d_4), 0.089.

Anal. Calcd for $C_9H_{10}D_2$: C, 88.45; H + D, 8.25 + 3.30 = 11.55. Found: C, 88.36; H + D, 11.49. Duplicate: C, 88.39; H + D, 11.47.

For the suspected 1-methyl-1-vinyl-1-(vinyl-2,2-d_2)-cyclobutene, ir (gas, NaCl): 3080, 3040, 3000, 2960, 2920, 2880, 2300 (w), 2220 (w), 1680, 1585, 1450, 990, 910; nmr (CCl_4): δ 1.63-1.84 (m, 3H), 2.30-2.43 (m, 2H), 4.62-5.18 (m, 4H), 5.58-6.24 (m, 3H).

Thermolysis of 3-methylene-1-vinyl-1-(vinyl-2,2-d_2)-cyclobutane (2-d_2); Intramolecular isotope effect

A 5% solution of (2-d_2) in benzene was prepared, sealed in a large capillary tube (bore, 5 mm), and pyrolyzed at 121.5° for 5 hr. A sample of (2) was subjected to the same conditions and was used as a control. Gas chromatography on a 5' (18%) DC-200 column at 70° was used to separate solvent from product. The product was then taken up in $CDCl_3$, and a nmr spectrum was taken. Two separate determinations were possible from a 100 MHz nmr spectrum. One involved the continuous-sweep integrations of the aliphatic region with the determination of the ratio of the allylic H/diallylic H or H_a/H_b. The other involved the continuous-sweep integrations of the vinylic region with the determination of the ratio of terminal-vinyl H/vinyl-ring H or $(H_c + H_d)/H_e$.

Calculation of the intramolecular isotope effect from the aliphatic region in the nmr of the mixture of the dideuterated sample of (3a + 3b)

$$H_a/H_b = 2.00(F_{3a}) + 1.00(F_{3b}) + 1.25(F_{3\text{-}d_3}) + 1.00(F_{3\text{-}d_4})$$

$$H_a/H_b = 2.00(F_{\underline{3a}}) + 1.00(F_{\underline{3b}}) + 1.25(0.050) + 1.00(0.089)$$

$$1.465^* = 2.00(F_{\underline{3a}}) + 1.00(F_{\underline{3b}}) + 0.1515$$

$$1.313 = 2.00(F_{\underline{3a}}) + 1.00(F_{\underline{3b}})$$

But $F_{\underline{3a}} + F_{\underline{3b}} = 0.861$ or $F_{\underline{3b}} = 0.861 - F_{\underline{3a}}$

Thus $F_{\underline{3a}} = 0.4525$ and $F_{\underline{3b}} = 0.4085$

Thus $F_{\underline{3a}}/F_{\underline{3b}} = 0.4525/0.4085 = 1.11$

* See Table 3.

Calculation of the intramolecular isotope effect from the vinylic region in the nmr of the mixture of the dideuterated sample of (3a + 3b)

$$(H_c + H_d)/H_e = 2.00(F_{\underline{3a}}) + 4.00(F_{\underline{3b}}) + 2.50(F_{\underline{3}\text{-}\underline{d}_3}) + 2.00(F_{\underline{3}\text{-}\underline{d}_4})$$

$$(H_c + H_d)/H_e = 2.00(F_{\underline{3a}}) + 4.00(F_{\underline{3b}}) + 2.50(0.050) + 2.00(0.089)$$

$$2.818^* = 2.00(F_{\underline{3a}}) + 4.00(F_{\underline{3b}}) + 0.303$$

$$1.257 = 1.00(F_{\underline{3a}}) + 2.00(F_{\underline{3b}})$$

But $F_{\underline{3a}} + F_{\underline{3b}} = 0.861$ or $F_{\underline{3a}} = 0.861 - F_{\underline{3b}}$

Thus $F_{\underline{3b}} = 0.3965$ and $F_{\underline{3a}} = 0.4645$

Thus $F_{\underline{3a}}/F_{\underline{3b}} = 0.4645/0.3965 = 1.17$

* See Table 4.

Table 3

Nmr integrations in the aliphatic region of the product mixture of (3a + 3b)

Runs	Area of H_a	Area of H_b	(H_a/H_b)*
1	55.0	35.0	1.571-0.018
2	56.0	34.5	1.623+0.033
3	57.0	36.0	1.583+0.007
4	56.5	35.0	1.614+0.024
5	56.0	35.0	1.600+0.010
6	55.5	34.5	1.609+0.019
7	55.0	34.5	1.594+0.004
8	54.0	34.5	1.565-0.025
9	54.0	34.5	1.565-0.025
10	54.0	34.5	1.565-0.025
11	55.0	34.5	1.594+0.004
12	55.0	34.5	1.594-0.004
		Average:	1.590±0.016*

* For the control sample, H_a/H_b = 2.170±0.027 (should be 2.000), so that the actual ratio of H_a/H_b in the dideuterated sample is 1.465±0.016.

Table 4

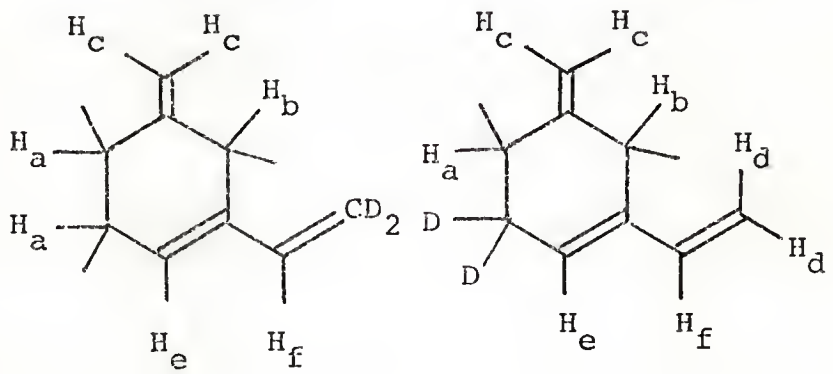
Nmr integrations in the vinylic region of the product mixture of (3a + 3b)

Runs	Area of $(H_c + H_d)$	Area of H_e	$(H_c + H_d)/H_e$*
1	55.0	18.0	3.056-0.024
2	54.5	17.5	3.114+0.035
3	55.5	18.5	3.000-0.079
4	56.0	18.0	3.111+0.032
5	54.5	17.5	3.111+0.032
6	55.0	18.0	3.056-0.024
7	57.0	19.0	3.000-0.079
8	53.5	17.5	3.057-0.022
9	55.5	17.5	3.171+0.092
10	55.0	17.5	3.143+0.063
11	55.0	18.0	3.056-0.024
		Average:	3.079±0.046*

* For the control sample, $(H_c + H_d)/H_e = 4.372 \pm 0.038$ (should be 4.000), so that the actual ratio of $(H_c + H_d)/H_e$ in the dideuterated sample is 2.818±0.046.

Table 5

Intramolecular isotope effect results for the rearrangement of (2-d_2) to (3a) and (3b)



Protons	Nmr integration ratio	(3a/3b) or (k_H/k_D)
H_a/H_b	1.465±0.016[a]	1.11±0.06[b]
$(H_c + H_d)/H_e$	2.818±0.046[a]	1.17±0.09[b]
	Average:	1.14±0.07

a Corrected to the control run.

b Corrected for isotopic isomer contamination.

3-Methylenecyclobutanecarbonitrile (43)[30]

A 1.4 l. stainless steel rocker autoclave was charged with 230.0 g (4.25 mol) of freshly distilled acrylonitrile, 200 ml dry toluene, 50.0 g (1.25 mol) of allene, and 2.0 g of hydroquinone. The autoclave was heated to 220° for 16 hr with agitation and under autogenous pressure. After cooling to room temperature, the autoclave was opened, and the product mixture was freed from toluene and unreacted acrylonitrile. The product was fractionally distilled at 64.5-65.0°/21 mm (lit.[30] 64-65°/21 mm), collecting 57.0 g (59%). Ir (neat, NaCl): 3000, 2350, 1440, 885; nmr (CCl_4): δ 2.92-3.34 (m, 5H), 4.75-5.05 (m, 2H); mass spectrum: m/e 93 (M^+).

3-Methylenecyclobutanecarboxylic acid (44)[30]

In a 1 l. one-necked flask, 93.5 g of 87% KOH was dissolved in 670 ml of 50% ethanol. To this, a total of 33.3 g (0.357 mol) of (43) was added in one portion. The reaction mixture was refluxed on a steam bath for 4 hr. The carboxylic acid salt was freed from the solvents by rotary evaporation and then redissolved in 150 ml of water and 2 ml of benzene. Again the solvents were removed from the carboxylic acid salt by rotary evaporation. The carboxylic acid salt was then dissolved in 200 ml of water, cooled to 0°, and hydrolyzed with conc. HCl to a pH ≈ 1. The product was extracted with 4 x 100 ml portions of ether and dried over Na_2SO_4 overnight. The product was

fractionally distilled at 105-106°/10 mm (lit.[30] 99-101°/ 9 mm), collecting 34.0 g (93%) of a colorless liquid. Ir (neat, NaCl): 2950, 1700, 1410, 1320, 1290, 1240, 1200, 1040, 935, 885, 785, 690; nmr (CCl_4): δ 2.72-3.33 (m, 5H), 4.65-4.96 (m, 2H), 0.00 (s, 1H); mass spectrum: m/e 112 (M^+).

3-Methylenecyclobutylcarbinol (45)

In a 2 l. three-necked flask, 20.0 g (0.526 mol) of $LiAlH_4$ was well stirred with 1000 ml of dry ether. To this over a 3-hr period, 49.6 g (0.442 mol) of (44) was added dropwise at 25°. The pot contents were gently refluxed for 20 hr and then cooled to 0°, prior to hydrolysis with 20 ml of water, 20 ml of 15% of NaOH solution, and 20 ml of water. The product mixture was filtered, and the ether solution was dried with Na_2SO_4 overnight. In addition, the lithium salts were subjected to Soxhlet extraction with refluxing ether, and this too was dried over Na_2SO_4 overnight. Once freed from ether, the dry product was fractionally distilled at 101-103°/78 mm, yielding 41.2 g (95%). Ir (neat, NaCl): 3300, 2900, 1670, 1410, 1040, 1020, 975, 900, 880; nmr (CCl_4): δ 2.10-3.10 (m, 5H), 3.50 (s, 1H), 3.60 (s, 1H), 4.44 (s, 1H), 4.62-4.82 (m, 2H); mass spectrum: m/e 98 (M^+).

3-Methylenecyclobutylcarbinyl-p-toluenesulfonate (46)

In a 250 ml three-necked flask, 20.0 g (0.204 mol) of (45) in 40.0 g (0.508 mol) of dry pyridine[59] was well

stirred with an overhead stirrer and cooled to ca. -10° with an ice-salt bath. In small portions over a 90-min period, 48.8 g (0.255 mol) of finely powdered p-toluenesulfonylchloride was added through a solid addition tube. The system was continuously subjected to a dry argon flow throughout the reaction, and the pot temperature was always maintained below 5°. After addition of the tosylchloride was complete, the reaction mixture was stirred at below 0° for 45 min more and then warming to 25° gradually for 30 min. The resulting pasty material was poured into a vigorously stirred mixture of cracked ice and water. It was stirred until all the ice had melted and the paste solidified. The solid was filtered from ice water, recrystallized from absolute ethanol, and dried over full vacuum. The product weighed 50.2 g (98%). Mp: 40.5-41.5°; ir (KBr): 3000, 2900, 1910, 1670, 1590, 1490, 1460, 1360, 1190, 1180, 1120, 1100, 1020, 960, 880, 845, 815, 790, 775; nmr ($CDCl_3$): δ 2.40 (s, 3H), 2.10-2.90 (m, 5H), 4.00-4.10 (m, 2H), 4.68-4.85 (m, 2H), 7.57 (AB q, 4H); mass spectrum: m/e 252 (M^+).

3-Methylenecyclobutaneacetonitrile (47)

In a 500 ml three-necked flask, fitted with an overhead stirrer, a Friedrich condenser with a $CaCl_2$ dyring tube, a thermometer, and a pressure-equalizing dropping funnel, 51.5 g (0.795 mol) of KCN in 100 ml of dry DMSO was heated to ca. 65°, and a solution of 40.0 g (0.159 mol)

of (46) in 100 ml of DMSO was added dropwise over a 75-min period. During the addition the temperature was maintained between 65-75°, and afterwards the reaction mixture was heated additionally to 75° for 22 hr. The cooled pot contents were diluted with 800 ml of water. The aqueous DMSO solution was extracted with 600 ml of pentane, and this extract was washed with water and dried over molecular sieves 3A. The product was purified by fractional distillation at 104.5-106.5°/57 mm, yielding 11.5 g (68%). Ir (neat, NaCl): 3050, 2900, 2250, 1670, 1430, 1410, 1390, 1340, 1200, 885; nmr (CCl_4): δ 2.76-3.87 (m, 7H), 4.73-4.92 (m, 2H); mass spectrum: m/e 107 (M^+).

3-Methylenecyclobutylacetic acid (48)

In a 500 ml one-necked flask, 28.9 g of 87% KOH was dissolved in 250 ml of 50% ethanol. To this, 11.0 g (0.103 mol) of (47) was added in one portion, and the solution was then heated to reflux for 4 hr. The aqueous ethanol was removed completely by rotary evaporation under 30 mm pressure, and the residual solid was redissolved in 100 ml of water, cooled to 0°, and hydrolyzed with conc. HCl to a pH ≈ 1. The product was extracted with 500 ml of ether and dried overnight over Na_2SO_4. The product was fractionally distilled at 118-122°/17 mm, yielding 10.5 g (81%). Ir (neat, NaCl): 3100, 2900, 2650, 1710, 1670, 1430, 1410, 1305, 1280, 1210, 1130, 940, 880;

nmr (CCl_4): δ 2.00-3.20 (m, 7H), 4.62-4.85 (m, 2H), 12.72 (s, 1H); mass spectrum: m/e 126 (M^+).

3-Methylenecyclobutylethanol (49)

In a 500 ml three-necked flask, 3.4 g (0.090 mol) of $LiAlH_4$ was well stirred with 180 ml of dry ether. To this over a 75-min period, 9.0 g (0.080 mol) of (48) was added dropwise at ca. 25°. The pot contents were gently refluxed for 19 hr and then cooled to 0°, prior to hydrolysis with 4 ml of water, 4 ml of 15% NaOH solution, and 4 ml of water. The product mixture was then filtered, and the ether solution was dried with Na_2SO_4 overnight. The product was fractionally distilled at 89.0-91.5°/22 mm, giving 6.3 g (70%) of product. Ir (neat, NaCl): 3300, 3050, 2900, 1670, 1400, 1055, 875; nmr (CCl_4): δ 1.48-1.93 (m, 2H), 2.00-2.10 (m, 5H), 3.42-3.67 (m, 3H), 4.51-4.85 (m, 2H); mass spectrum: m/e 112 (M^+).

3-Methylenecyclobutylethanol-p-toluenesulfonate (50)

In a 50 ml three-necked flask, 3.0 g (0.027 mol) of (49) in 5.3 g (0.067 mol) of dry pyridine[59] was well stirred with magnetic stirring bar and cooled to ca. -10° with an ice-salt bath. In small portions, 6.4 g (0.034 mol) of p-toluenesulfonylchloride was added through a solid addition funnel over a 15-min period. The system was continuously subjected to a dry argon flow throughout the reaction, and the the pot temperature was always maintained around 0°. When addition was complete, the reaction mixture was

stirred at below 0° for 75 min more and then warming to 25° for only 15 min. The resulting pasty material could not be solidified when poured into a vigorously stirred cracked ice and water mixture, so that the resulting oil was taken up in ether, washed with 200 ml of 3% $NaHCO_3$ solution and 100 ml of water, and then dried over molecular sieves 3A for 4 hr. Once freed from ether, the product weighed 6.0 g (84%) which was used without further purification for spectral data and for use in the following reaction. Ir (neat, NaCl): 3050, 2950, 1670, 1600, 1360, 1190, 1180, 940, 880; nmr ($CDCl_3$): δ 1.55-3.00 (m, 7H), 2.45 (s, 3H), 3.90-4.15 (t, 2H, J = 6.5 Hz), 4.60-4.82 (m, 2H), 7.57 (AB q, 4H); mass spectrum: m/e 266 (M^+).

Methylene-3-vinylcyclobutane (29)

A 250 ml three-necked flask was fitted with a pressure-equalizing dropping funnel, a magnetic stirring bar, and a bent tube connected to a coiled trap through which a vacuum pump was connected. The flask was charged with 4.6 g (0.041 mol) of potassium-t-butoxide. To this, a solution of 6.0 g (0.023 mol) of (50) in 40 ml of freshly dried DMSO[60] was added dropwise over a 35-min period under 25 mm vacuum and with the coiled trap cooled by liquid nitrogen. Immediately after addition, the vacuum was increased to 0.75 mm and held there for 8 hr. The volatile compounds, collected in the coiled trap, were transferred under full vacuum to a small, more accessible tube via vacuum line

and sealed until purification could be accomplished. Gas chromatography on a 5' (18%) DC-200 column at 60° afforded 0.43 g (20%) of a pure product. Ir (gas, NaCl): 3090, 2950, 1680, 1645, 1420, 990, 920, 915, 880; nmr (CCl_4): δ 2.33-3.12 (m, 5H), 4.65-4.95 (m, 3H), 4.97-5.18 (m, 1H), 5.80-6.40 (m, 1H); mass spectrum: m/e 94 (7.7), 93 (25.6), 91 (17.9), 80 (12.8), 79 (100), 78 (7.7), 77 (41.0), 67 (5.1), 66 (20.5), 65 (10.3), 55 (7.7), 54 (66.7), 53 (23.1), 51 (12.8), 43 (15.4), 42 (7.7), 41 (12.8), 40 (15.4), 39 (56.4).

Anal. Calcd for C_7H_{10}: C, 89.29; H, 10.71. Found: C, 89.13; H, 10.77.

4-Methylenecyclohexene (30)[33]

In four 1 ml tubes, 400 µl each of 5% of (29) in n-decane was transferred by syringe and sealed under vacuum. A protective wire gauze sleeve was placed around each tube and subsequently heated to 210° for 15 hr. Purification was accomplished by gas chromatography on a 5' (18%) DC-200 column at 65°. The reaction was quantitative and clean. Ir (gas, NaCl): 2980, 2890, 1640, 1430, 890; nmr (CCl_4): δ 2.21 (s, 4H), 2.72 (s, 2H), 4.68 (s, 2H), 5.62 (s, 2H); mass spectrum: m/e 95 (7.2), 94 (76.7), 93 (20.9), 92 (4.7), 91 (30.5), 80 (9.6), 79 (100), 78 (15.8), 77 (56.8), 67 (5.1), 66 (13.7), 65 (11.0), 55 (6.2), 54 (11.0), 53 (15.8), 52 (6.8), 51 (15.4) 50 (9.6).

Kinetic analysis for methylene-3-vinylcyclobutane (29)

A solution of ca. 5% of methylene-3-vinylcyclobutane (29) in ca. 95% of high purity n-decane[61] was prepared in a 10 ml tube. From this homogeneous solution, 25 µl aliquots were extracted and transferred by syringe to 6" capillary tubes (O. D. = 7 mm; bore, 1.0-1.5 mm). The capillary tubes were sealed under vacuum with the contents cooled by liquid nitrogen prior to evacuation. In this manner, forty tubes were readied for kinetic runs. Each capillary tube, prior to immersion in the hot oil, was protected by a well-fitting wire gauze sleeve. The tubes were heated in a well-insulated and well-stirred oil bath, a Lauda constant temperature circulator type N/S15/12, equipped with an R-10 electronic relay, an R-20 electronic controller, and a R-30 temperature and level protection relay, and filled with Ultra-Therm 330S silicone fluid. Temperatures were monitored both by a thermometer, calibrated in 0.1°, and by using a calibrated chromel-alumel thermocouple in conjunction with a Honeywell model 2702 potentiometer. Six or seven prepared tubes were used per temperature run. Each tube was withdrawn from the oil bath at an appropriate time, cooled immediately by a dry ice-isopropanol bath, opened, and analyzed by gas chromatography on a 7.5' (2%) DC-200 column at 50°. The kinetic analyses were performed on a Hewlett-Packard model 5710A gas chromatograph with a flame ionization detector. The chemical composition of the kinetic samples was

determined with a Vidar Autolab 6300 digital integrator. A first-order, least squares program[62] was used in conjunction with a pdp 8/e digital computer to analyze all the data (see Appendix I). Rate constants at six different temperatures were determined and compiled in Table 6.

Table 6

Kinetics for the thermal rearrangement of (29) to (30)

Temp (°C)	Temp (°K)	10^{-3}/Temp (°K)	k x 10^{5} sec
175.00	448.15	2.2314	1.97±0.02
182.00	455.15	2.1971	3.80±0.03
187.75	460.90	2.1697	6.23±0.04
196.25	469.40	2.1304	12.6 ±0.8
202.25	475.40	2.1035	20.6 ±0.3
211.00	484.15	2.0655	38.5 ±0.2

A computer program was formulated to produce an Arrhenius plot of log k = log A - E_a/RT for this first-order reaction,[62] and it also calculated the appropriate parameters. An Arrhenius plot for these data appears in Figure 5. Energy of activation, 35.67±0.41 kcal/mol; log A, 12.70±0.19; enthalpy of activation, 34.74±0.41 kcal/mol at 192.3°; entropy of activation, -3.29±0.87 cal/mol-deg at 192.3°; free energy of activation,

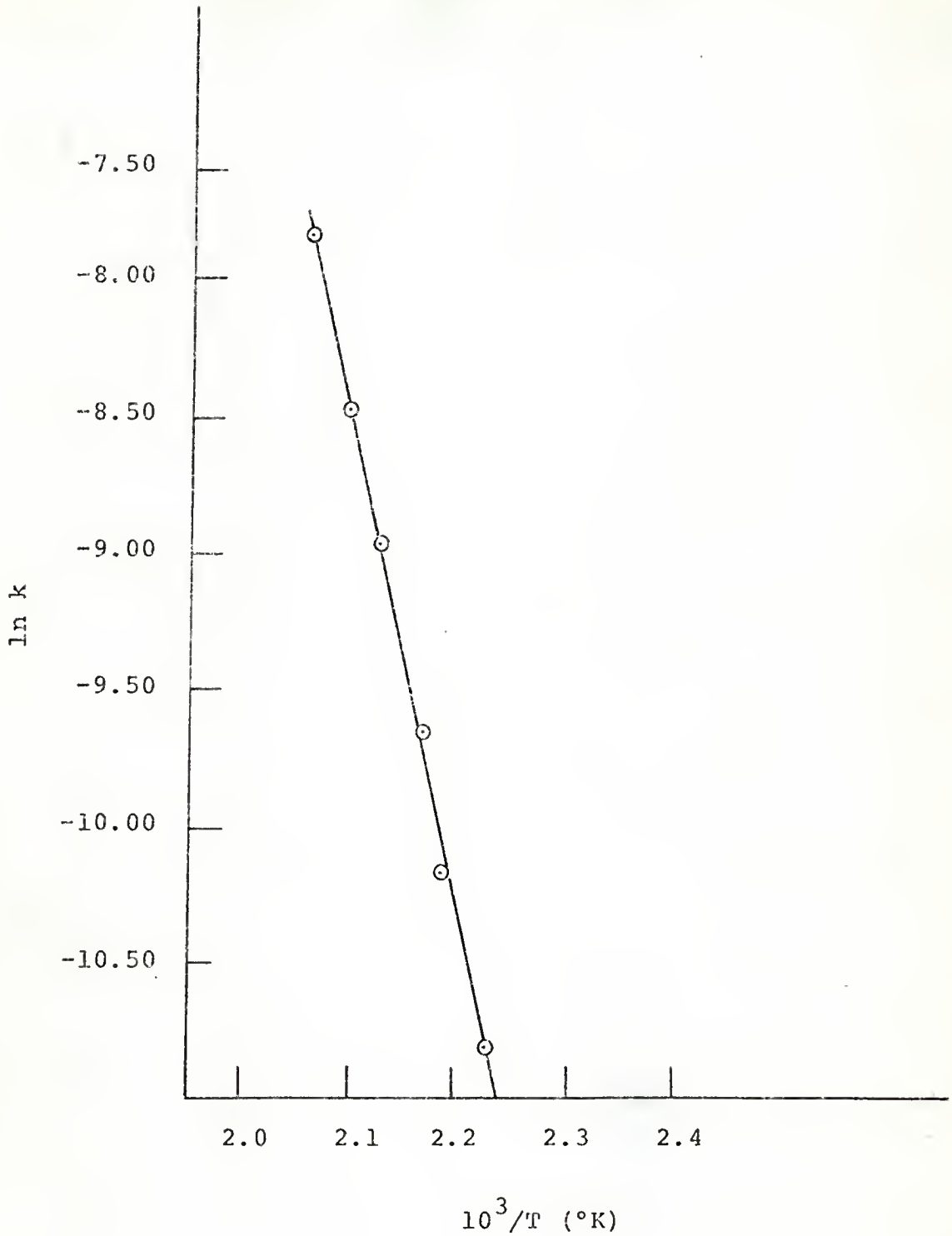


Figure 5: Arrhenius plot for the conversion of (29) to (30)

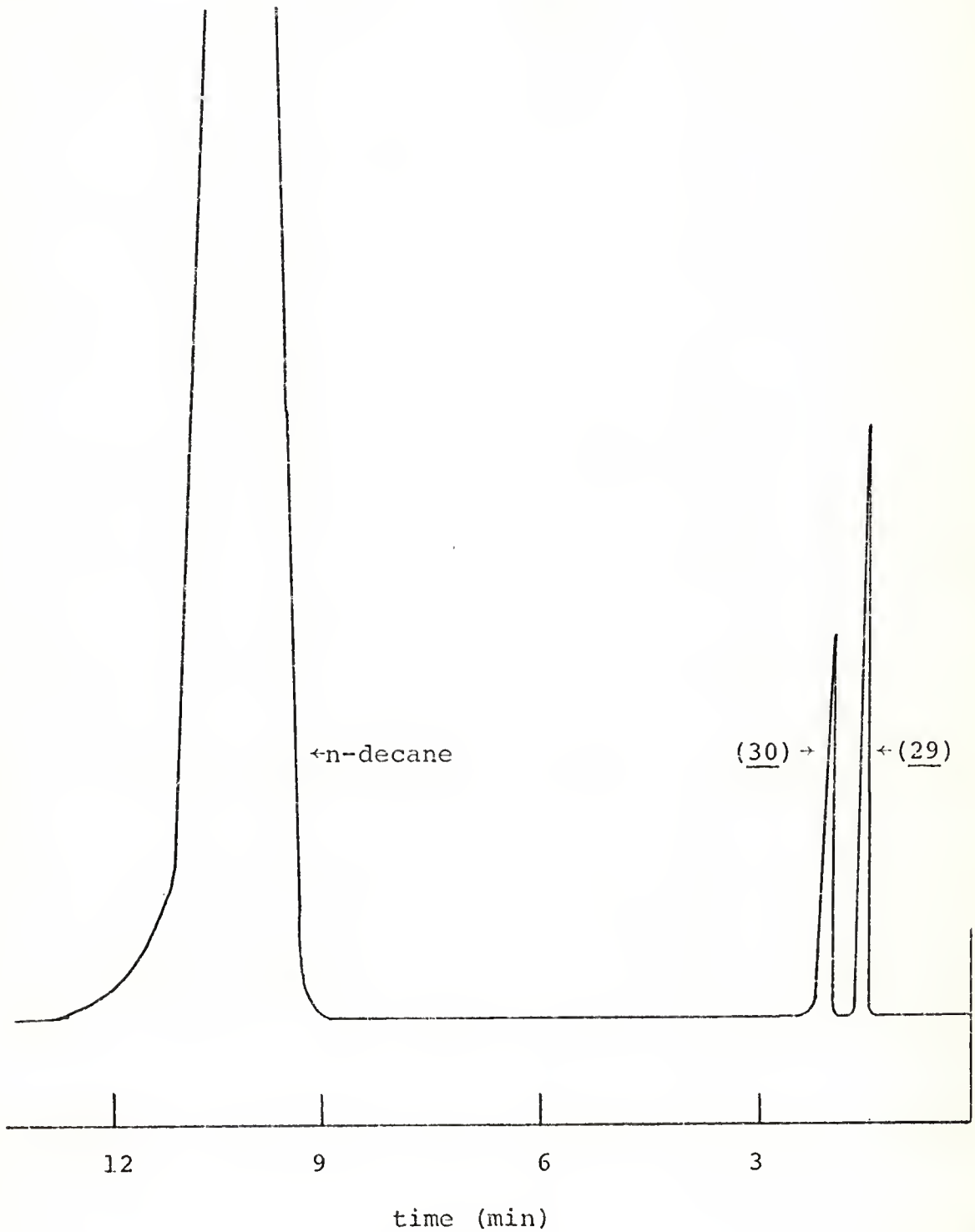


Figure 6: Sample glpc trace of the kinetic analysis for the thermal conversion of (29) to (30)

36.28±0.87 kcal/mol at 192.3°. The correlation coefficient was 0.9998.

APPENDIX I

A detailed compilation of the kinetic data on concentration versus time is presented in Tables 7 through 9. Table 7 includes the kinetic data for the pyrolysis of 1,1-divinyl-3-methylenecyclobutane (2). Table 8 includes the kinetic data for the pyrolysis of 1,1-di(vinyl-2,2-d_2)-3-methylenecyclobutane (2-d_4), and Table 9 includes the kinetic data on the pyrolysis of methylene-3-vinylcyclobutane (29). Under each temperature run, time is listed in seconds. The ratio is a ratio of 1,1-divinyl-3-methylenecyclobutane (2) or 1,1-di(vinyl-2,2-d_2)-3-methylenecyclobutane (2-d_4) to chromatographic quality n-nonane. For the thermolysis of methylene-3-vinylcyclobutane (29) to 4-methylenecyclohexene (30), the ratio represents a ratio of (29) to (29)/[(29) + (30)] at time t. The listing, deviation, is the computer calculation of the deviation of the observed ln ratio (also tabulated) with that which would be expected if the point lay precisely on a perfectly straight line. This deviation provides an indication for the goodness of fit of each point in these first-order reactions. The rate constant (in sec^{-1}), the intercept, and the correlation coefficient were also determined by a

least squares method computer analysis. A concentration versus time plot comparison was constructed in Figures 7 and 8 for the kinetic runs of (2) and (2-d_4) at 99.9° and 121.1°, temperatures at which intermolecular isotope effects were measured.

Table 7

Pyrolysis of 1,1-divinyl-3-methylenecyclobutane (2)

At 86.1°

Point	Time	Ratio	Ln ratio	Deviation
1	0	0.8224±0.0156	-0.1956	-0.0339
2	17541	0.6182±0.0058	-0.4810	0.0192
3	24008	0.5342±0.0100	-0.6270	-0.0021
4	34663	0.4336±0.0092	-0.8357	-0.0053
5	50256	0.3425±0.0036	-1.0714	0.0599
6	66607	0.2373±0.0060	-1.4384	0.0084
7	99729	0.1155±0.0053	-2.1586	-0.0728
8	135000	0.0646±0.0035	-2.7397	0.0266

Rate constant: $1.9293 \pm 0.0361 \times 10^{-5}$; intercept: -0.1617±0.0246; correlation coefficient: 0.9990.

At 93.2°

Point	Time	Ratio	Ln ratio	Deviation
1	0	0.8224±0.0156	-0.1956	-0.0321
2	6788	0.6308±0.0112	-0.4607	-0.0199
3	13920	0.4967±0.0058	-0.6998	0.0324
4	21120	0.3653±0.0033	-1.0072	0.0192
5	31824	0.2407±0.0064	-1.4241	0.0396
6	42665	0.1453±0.0093	-1.9289	-0.0222
7	60689	0.0699±0.0034	-2.6602	-0.0171

Rate constant: $4.0859 \pm 0.0618 \times 10^{-5}$; intercept: -0.1635 ± 0.0198; correlation coefficient: 0.9994.

At 99.9°

Point	Time	Ratio	Ln ratio	Deviation
1	0	0.8224±0.0156	-0.1956	-0.0023
2	1685	0.7276±0.0112	-0.3180	0.0026
3	3398	0.6258±0.0169	-0.4688	-0.0187
4	5206	0.5693±0.0081	-0.5633	0.0234
5	6857	0.4906±0.0103	-0.7122	-0.0007
6	8403	0.4441±0.0116	-0.8177	0.0166
7	11513	0.3430±0.0048	-1.0701	-0.0067
8	15652	0.2426±0.0037	-1.4163	-0.0402
9	19829	0.1893±0.0057	-1.6640	0.0272
10	24347	0.1308±0.0053	-2.0340	-0.0013

Rate constant: $7.5569 \pm 0.0877 \times 10^{-5}$; intercept: -0.1933 ± 0.0108; correlation coefficient: 0.9995.

At 100.7°

Point	Time	Ratio	Ln ratio	Deviation
1	0	0.8224±0.0156	-0.1956	0.0053
2	348	0.7577±0.0191	-0.2775	-0.0475
3	1685	0.7074±0.0175	-0.3462	-0.0045
4	4327	0.5991±0.0238	-0.5124	0.0504
5	5719	0.4950±0.0031	-0.7032	-0.0240
6	7058	0.4627±0.0058	-0.7708	0.0204

Point	Time	Ratio	Ln ratio	Deviation
7	8416	0.4146±0.0071	-0.8805	0.0242
8	9786	0.3463±0.0038	-1.0604	-0.0411
9	11116	0.3394±0.0116	-1.0805	0.0501
10	12745	0.2749±0.0055	-1.2912	-0.0243
11	14254	0.2616±0.0111	-1.3411	0.0520
12	16801	0.1881±0.0060	-1.6710	-0.0649
13	25204	0.0998±0.0053	-2.3049	0.0040

Rate constant: $8.3641 \pm 0.1636 \times 10^{-5}$; intercept: -0.2008±0.0186; correlation coefficient: 0.9979.

107.1°

Point	Time	Ratio	Ln ratio	Deviation
1	0	0.8224±0.0156	-0.1956	-0.0188
2	1201	0.6749±0.0083	-0.3933	-0.0188
3	2706	0.5378±0.0035	-0.6204	0.0018
4	5220	0.3497±0.0064	-1.0508	-0.0147
5	6501	0.3016±0.0083	-1.1986	0.0483
6	12001	0.1213±0.0043	-2.1093	0.0430
7	18026	0.0414±0.0012	-3.1849	-0.0408

Rate constant: $1.6462 \pm 0.0233 \times 10^{-4}$; intercept: -0.1767±0.0206; correlation coefficient: 0.9995.

At 114.6°

Point	Time	Ratio	Ln ratio	Deviation
1	0	0.8224±0.0156	-0.1956	0.0075
2	781	0.6439±0.0129	-0.4403	0.0043

Point	Time	Ratio	Ln ratio	Deviation
3	1445	0.5331±0.0093	-0.6290	0.0207
4	2219	0.4109±0.0046	-0.8894	-0.0004
5	3006	0.3271±0.0069	-1.1173	0.0150
6	4199	0.2133±0.0073	-1.5498	-0.0487
7	6300	0.1103±0.0048	-2.2047	-0.0541
8	8401	0.0643±0.0076	-2.7443	0.0557

Rate constant: $3.0911 \pm 0.0513 \times 10^{-4}$; intercept: -0.2031±0.0219; correlation coefficient: 0.9992.

At 121.1°

Point	Time	Ratio	Ln ratio	Deviation
1	0	0.8224±0.0156	-0.1956	-0.0171
2	276	0.6991±0.0092	-0.3580	-0.0200
3	486	0.6327±0.0072	-0.4578	0.0015
4	729	0.5568±0.0088	-0.5856	0.0142
5	968	0.4860±0.0038	-0.7216	0.0163
6	1202	0.4145±0.0130	-0.8807	-0.0076
7	1813	0.2931±0.0026	-1.2273	-0.0010
8	2417	0.2170±0.0062	-1.5279	0.0475
9	3602	0.1012±0.0069	-2.2909	-0.0305
10	4804	0.0519±0.0023	-2.9583	-0.0032

Rate constant: $5.7799 \pm 0.0503 \times 10^{-4}$; intercept: -0.1784±0.0111; correlation coefficient: 0.9997.

Table 8

Pyrolysis of 1,1-di(vinyl-2,2-d_2)-3-methylenecyclobutane (2-d_4)

At 99.9°

Point	Time	Ratio	Ln ratio	Deviation
1	0	0.4996±0.0015	-0.6939	-0.0118
2	1681	0.4453±0.0080	-0.8089	-0.0064
3	3371	0.3977±0.0070	-0.9222	0.0015
4	5040	0.3450±0.0043	-1.0641	-0.0208
5	6884	0.3161±0.0041	-1.1515	0.0240
6	8401	0.2766±0.0029	-1.2852	-0.0010
7	11766	0.2234±0.0055	-1.4988	0.0266
8	15127	0.1711±0.0031	-1.7653	0.0128
9	19583	0.1258±0.0046	-2.0729	0.0128
10	24103	0.0875±0.0019	-2.4357	-0.0260

Rate constant: $7.1677 \pm 0.0778 \times 10^{-5}$; intercept: -0.6821±0.0095; correlation coefficient: 0.9995.

At 121.1°

Point	Time	Ratio	Ln ratio	Deviation
1	0	0.4996±0.0015	-0.6939	-0.0560
2	304	0.4365±0.0067	-0.8289	-0.0227
3	506	0.3994±0.0064	-0.9178	0.0003
4	750	0.3522±0.0069	-1.0436	0.0097
5	975	0.3152±0.0028	-1.1544	0.0235

Point	Time	Ratio	Ln ratio	Deviation
6	1202	0.2824±0.0351	-1.2644	0.0393
7	1807	0.1980±0.0017	-1.6197	0.0191
8	2400	0.1428±0.0045	-1.9464	0.0209
9	4561	0.0408±0.0013	-3.1984	-0.0341

Rate constant: $5.5394 \pm 0.0841 \times 10^{-4}$; intercept: -0.6378±0.0161; correlation coefficient: 0.9992.

Table 9

Pyrolysis of methylene-3-vinylcyclobutane (29)

At 175.0°

Point	Time	Ratio	Ln ratio	Deviation
1	0	1.0000±0.0000	0.0000	0.0001
2	17446	0.7196±0.0067	-0.3290	0.0146
3	29668	0.5650±0.0049	-0.5709	0.0134
4	44294	0.4125±0.0027	-0.8856	-0.0133
5	61642	0.2864±0.0073	-1.2502	-0.0364
6	87962	0.1793±0.0020	-1.7188	0.0133
7	122740	0.0899±0.0013	-2.4087	0.0082

Rate constant: $1.9691 \pm 0.0198 \times 10^{-5}$; intercept: -0.0001±0.0129; correlation coefficient: 0.9997.

At 182.0°

Point	Time	Ratio	Ln ratio	Deviation
1	0	1.0000±0.0000	0.0000	-0.0148
2	8525	0.7277±0.0022	-0.3179	-0.0084
3	15446	0.5732±0.0110	-0.5566	0.0162
4	21769	0.4484±0.0044	-0.8022	0.0111
5	30692	0.3172±0.0030	-1.1483	0.0045
6	39874	0.2240±0.0045	-1.4961	0.0059
7	54812	0.1243±0.0046	-2.0848	-0.0145

Rate constant: $3.8041 \pm 0.0297 \times 10^{-5}$; intercept: 0.0148±0.0089; correlation coefficient: 0.9998.

At 187.75°

Point	Time	Ratio	Ln ratio	Deviation
1	0	1.0000±0.0000	0.0000	-0.0070
2	4276	0.7729±0.0036	-0.2577	0.0019
3	7619	0.6289±0.0056	-0.4638	0.0043
4	11043	0.5028±0.0010	-0.6875	-0.0060
5	16494	0.3670±0.0012	-1.0023	0.0190
6	21641	0.2592±0.0045	-1.3503	-0.0080
7	27031	0.1859±0.0045	-1.6826	-0.0043

Rate constant: $6.2346 \pm 0.0443 \times 10^{-5}$; intercept: 0.0070±0.0069; correlation coefficient: 0.9999.

At 196.25°

Point	Time	Ratio	Ln ratio	Deviation
1	0	1.0000±0.0000	0.0000	0.0017
2	3365	0.6539±0.0059	-0.4247	0.0027
3	5879	0.4716±0.0042	-0.7517	-0.0063
4	8506	0.3445±0.0048	-1.0658	0.0118
5	12643	0.2018±0.0012	-1.6004	0.0004
6	18000	0.0996±0.0020	-2.3065	-0.0281
7	24002	0.0488±0.0029	-3.0198	0.0178

Rate constant: $1.2649 \pm 0.0777 \times 10^{-4}$; intercept: -0.0017±0.0101; correlation coefficient: 0.9999.

At 202.25°

Point	Time	Ratio	Ln ratio	Deviation
1	0	1.0000±0.0000	0.0000	-0.0109
2	1505	0.7370±0.0031	-0.3052	-0.0061
3	2579	0.5981±0.0019	-0.5141	0.0062
4	3574	0.5038±0.0070	-0.6856	0.0395
5	5413	0.3292±0.0028	-1.1110	-0.0074
6	7240	0.2200±0.0035	-1.5140	-0.0341
7	10858	0.1095±0.0054	-2.2120	0.0128

Rate constant: $2.0591 \pm 0.0276 \times 10^{-4}$; intercept: 0.0109±0.0155; correlation coefficient: 0.9996.

At 202.25°

Point	Time	Ratio	Ln ratio	Deviation
1	0	1.0000±0.0000	0.0000	-0.0131
2	1505	0.7370±0.0031	-0.3052	-0.0075
3	2579	0.5981±0.0019	-0.5141	0.0054
4	3574	0.5038±0.0070	-0.6856	0.0393
5	5413	0.3292±0.0028	-1.1110	-0.0068
6	7240	0.2200±0.0035	-1.5140	-0.0322
7	10828	0.1095±0.0054	-2.2120	0.0128
8[a]	33509	0.0010±0.0000	-6.9067	-0.0015

Rate constant: $2.0646 \pm 0.0800 \times 10^{-4}$; intercept: -0.0353±0.0222; correlation coefficient: 0.9999.

a Calculated from the rate constant and half-life.

At 211.0°

Point	Time	Ratio	Ln ratio	Deviation
1	0	1.0000±0.0000	0.0000	-0.0076
2	576	0.8037±0.0079	-0.2185	-0.0041
3	913	0.7130±0.0060	-0.3383	0.0061
4	1327	0.6025±0.0071	-0.5067	-0.0028
5	1981	0.4701±0.0048	-0.7549	0.0009
6	2641	0.3668±0.0062	-1.0029	0.0073
7	3307	0.2850±0.0058	-1.2554	0.0115
8	5213	0.1336±0.0034	-2.0129	-0.0112

Rate constant: $3.8542 \pm 0.0189 \times 10^{-4}$; intercept: 0.0076±0.0048; correlation coefficient: 0.9999.

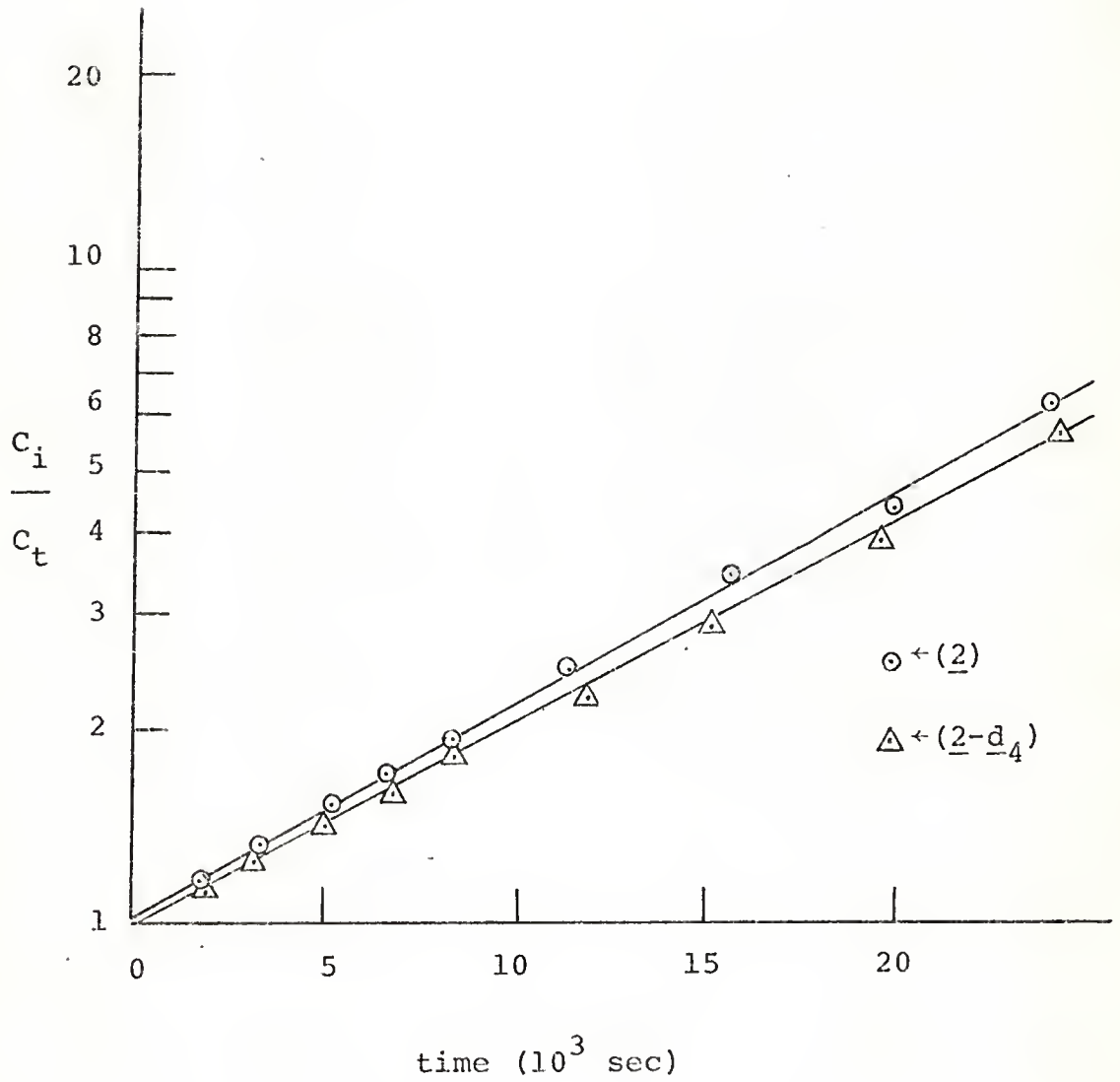


Figure 7: Concentration versus time plot comparison of compounds (2) and (2-d_4) at 99.9°

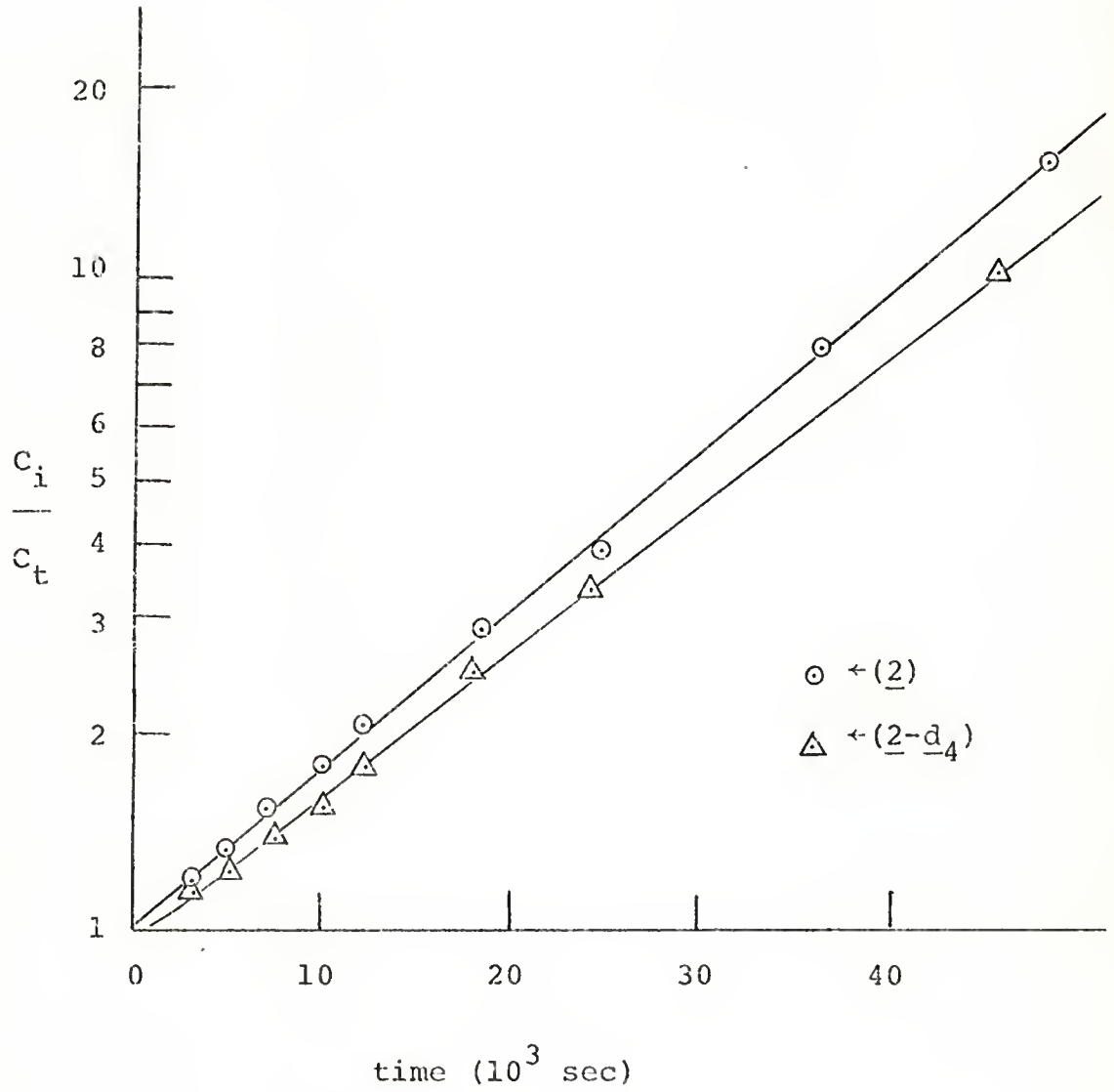


Figure 8: Concentration versus time plot comparison of compounds (2) and (2-d_4) at 121.1°

APPENDIX II

Nmr and ir spectra of (2), (3), (2-d_4), (3-d_4), (2-d_2), (3a + 3b), (29), and (30) are found herein.

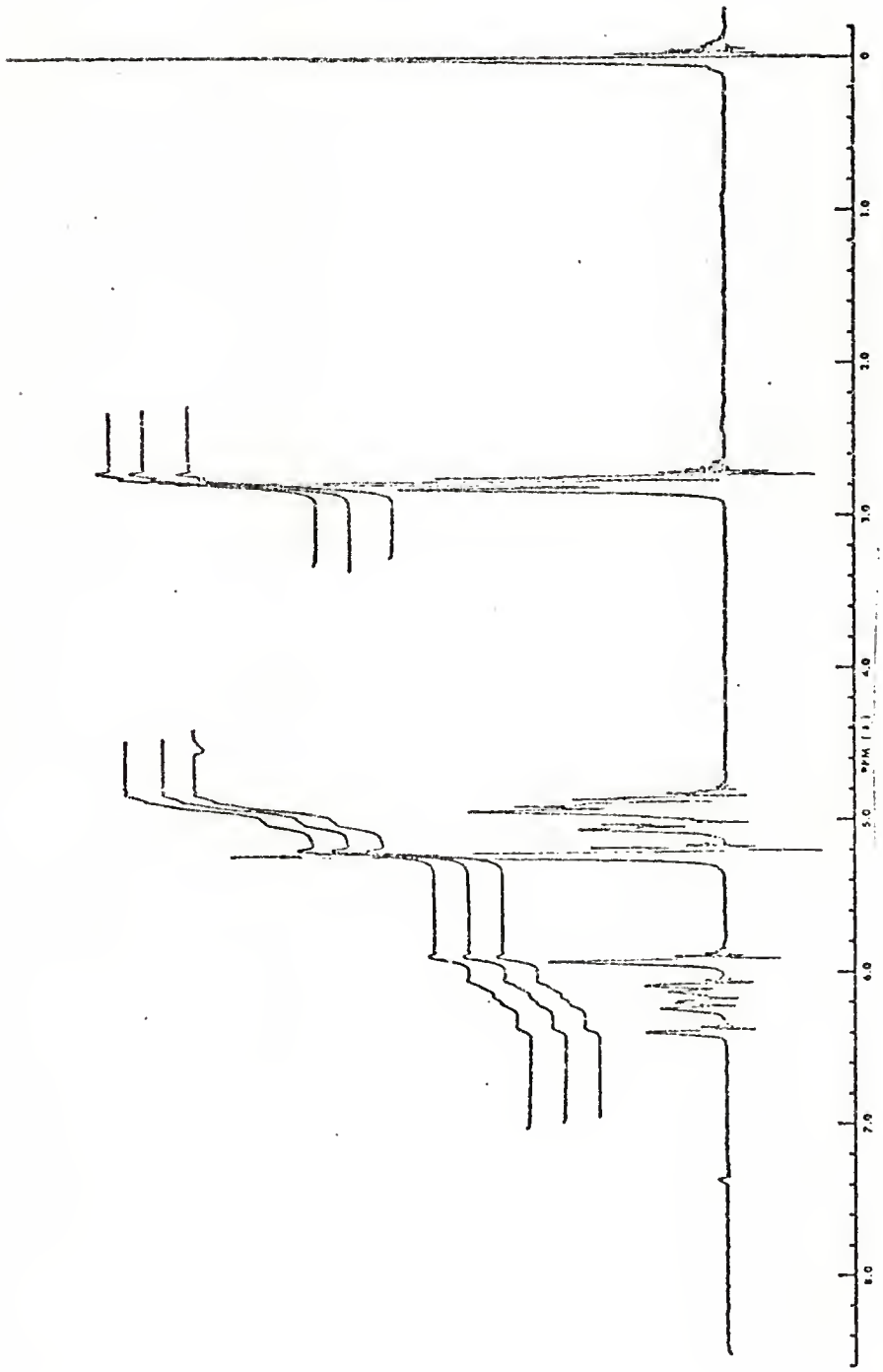


Figure 9: Nmr of 1,1-divinyl-3-methylenecyclobutane (2)

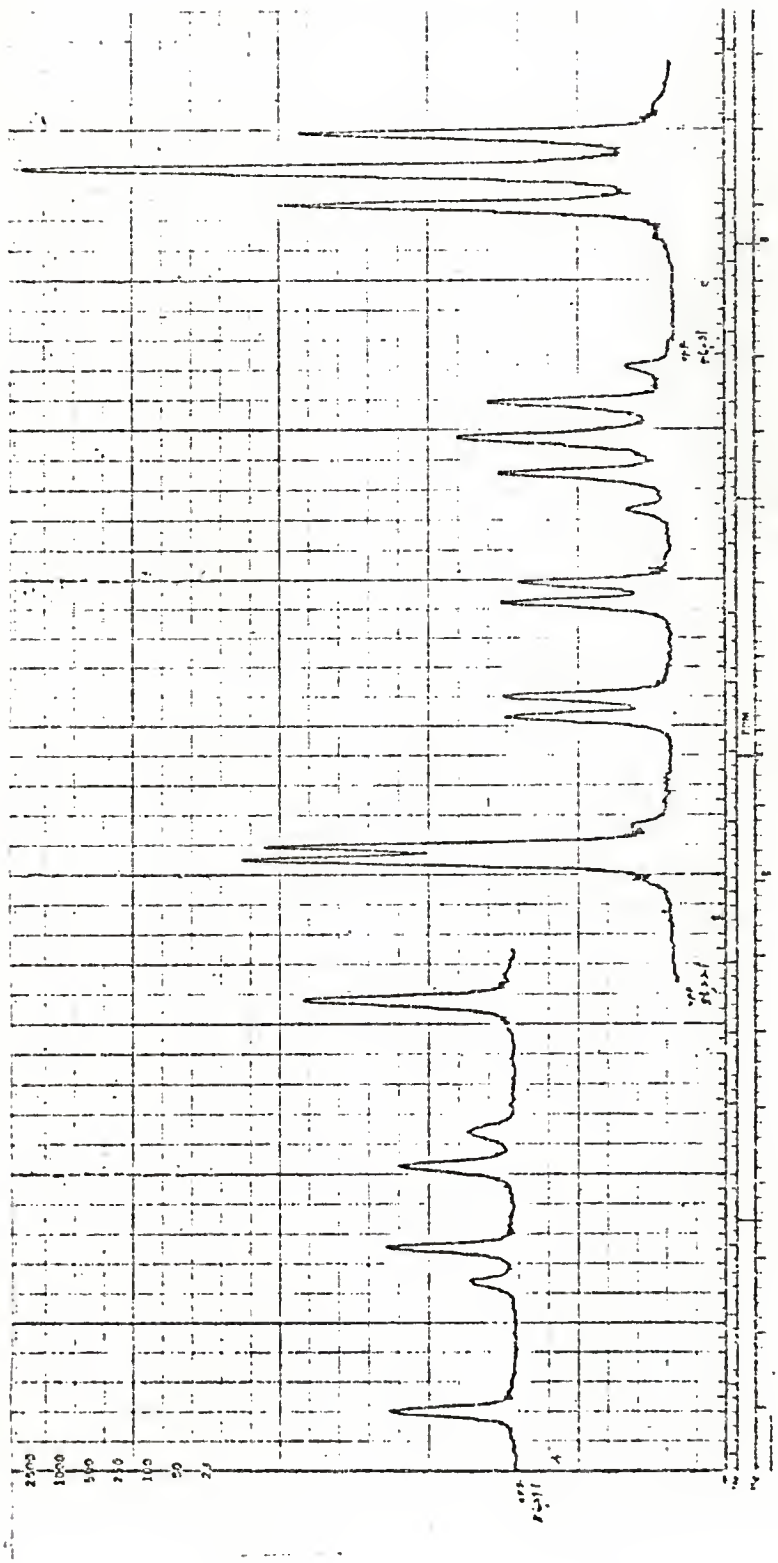


Figure 10: Nmr (100 MHz) at 100 cps sweep width of 1,1-divinyl-3-methylenecyclobutane (2)

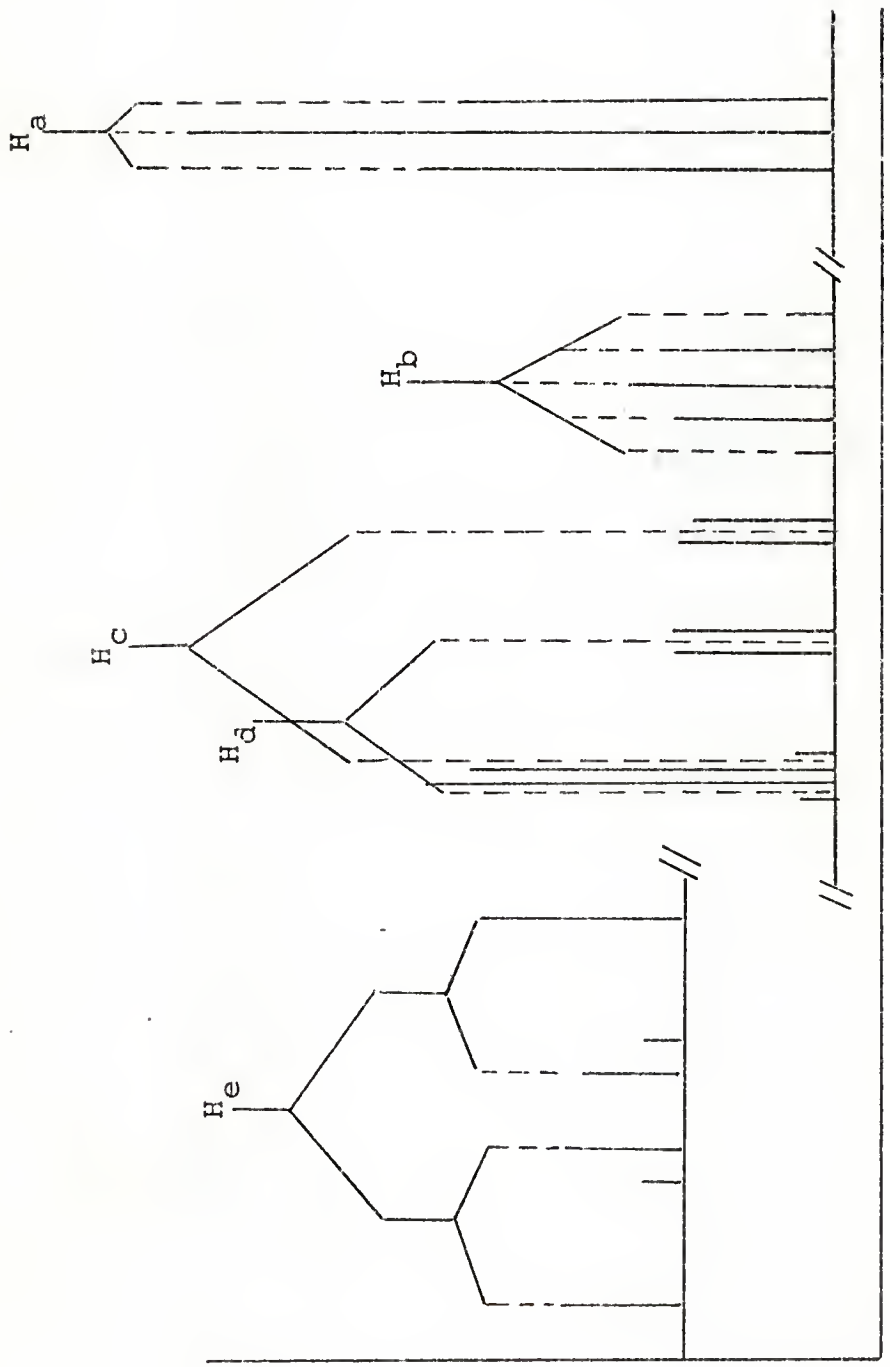


Figure 11: Line analysis for the nmr (100 MHz) at 100 cps sweep width of 1,1-divinyl-3-methylenecyclobutane (2)

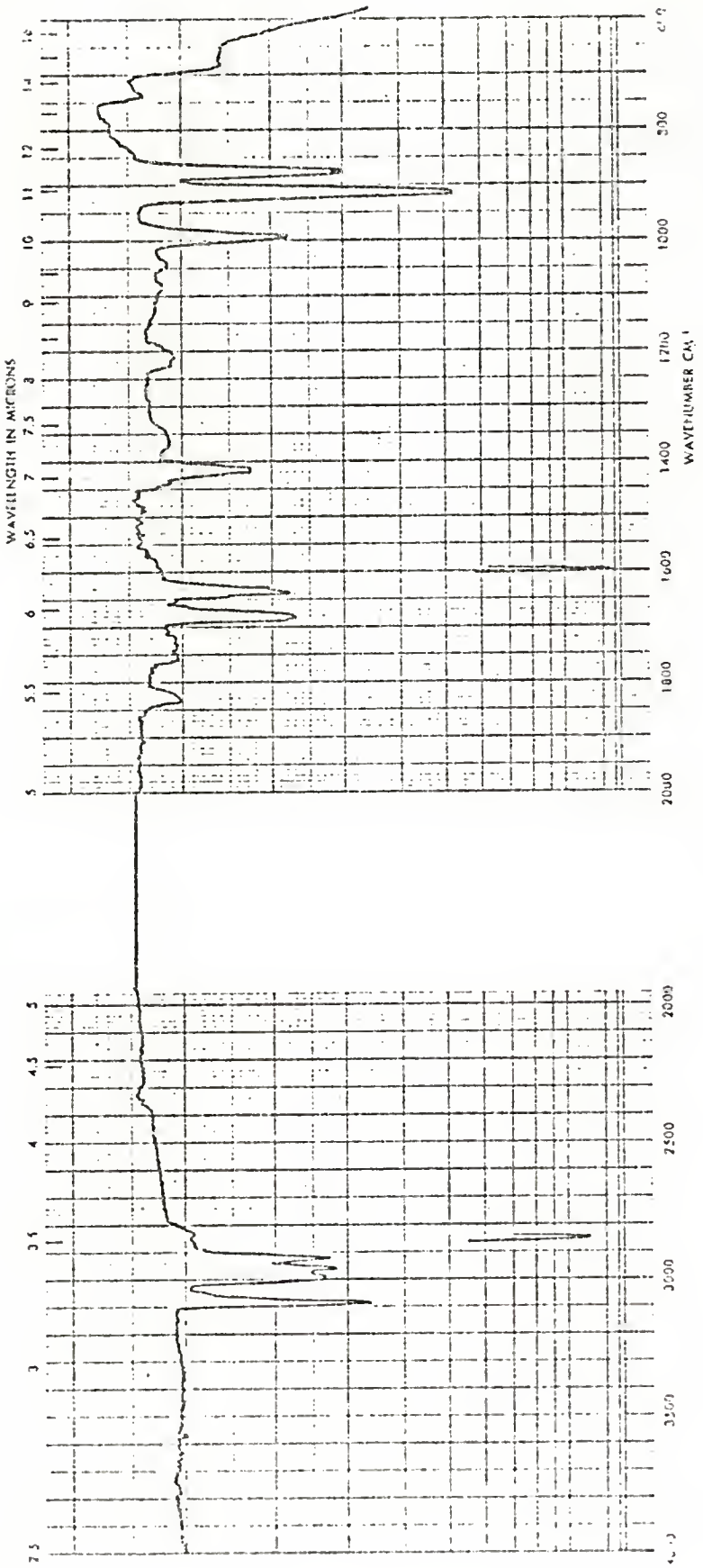


Figure 12: Ir of 1,1-divinyl-3-methylenecyclobutane (2)

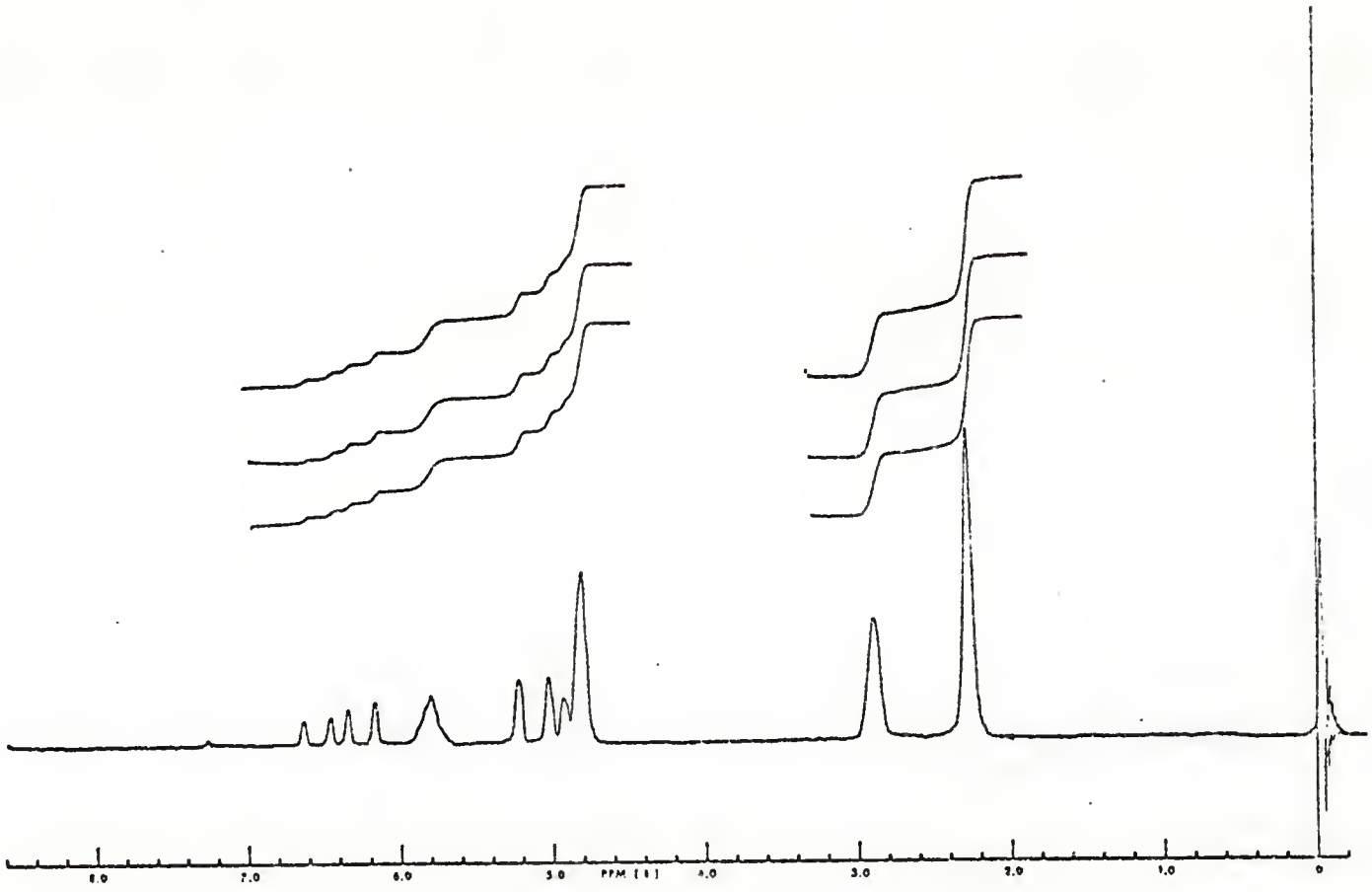


Figure 13: Nmr of 4-methylene-2-vinylcyclohexene (3)

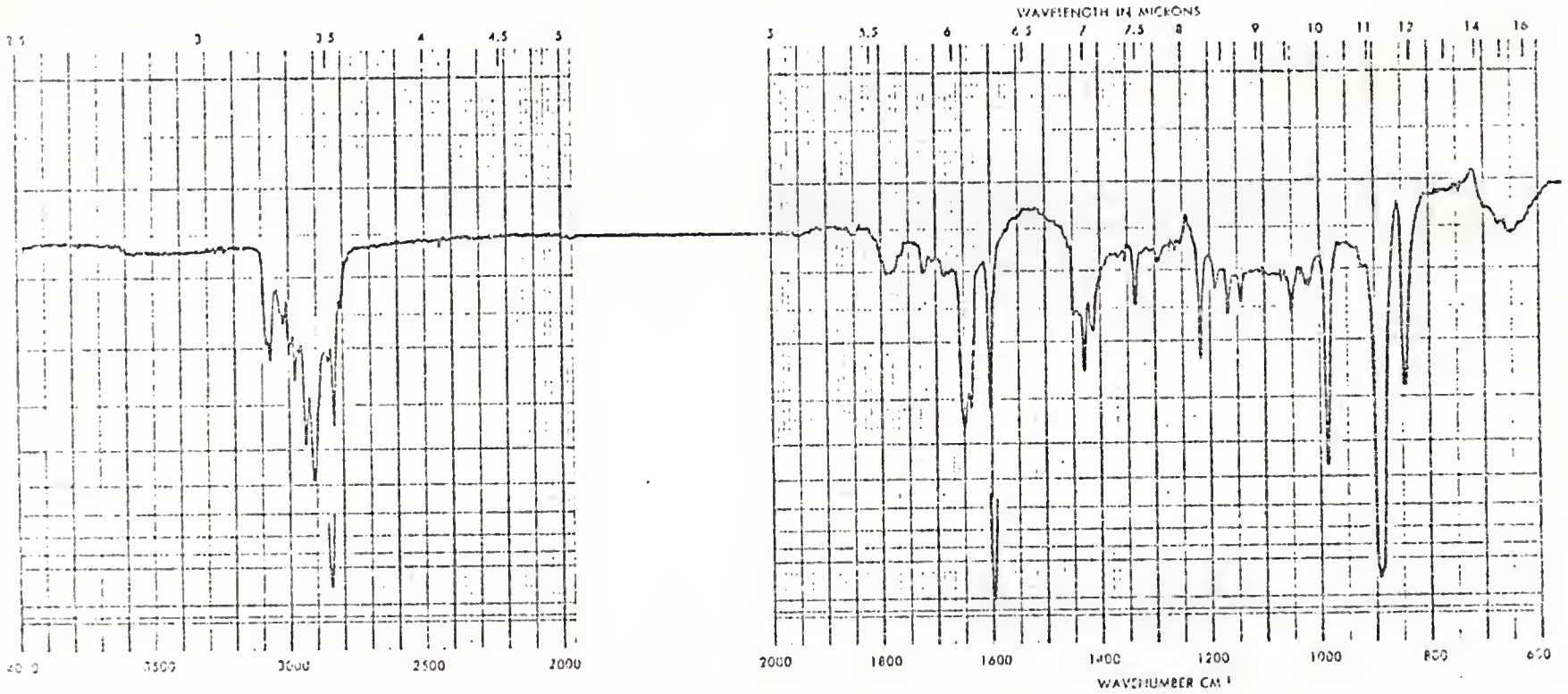


Figure 14: Ir of 4-methylene-2-vinylcyclohexene (3)

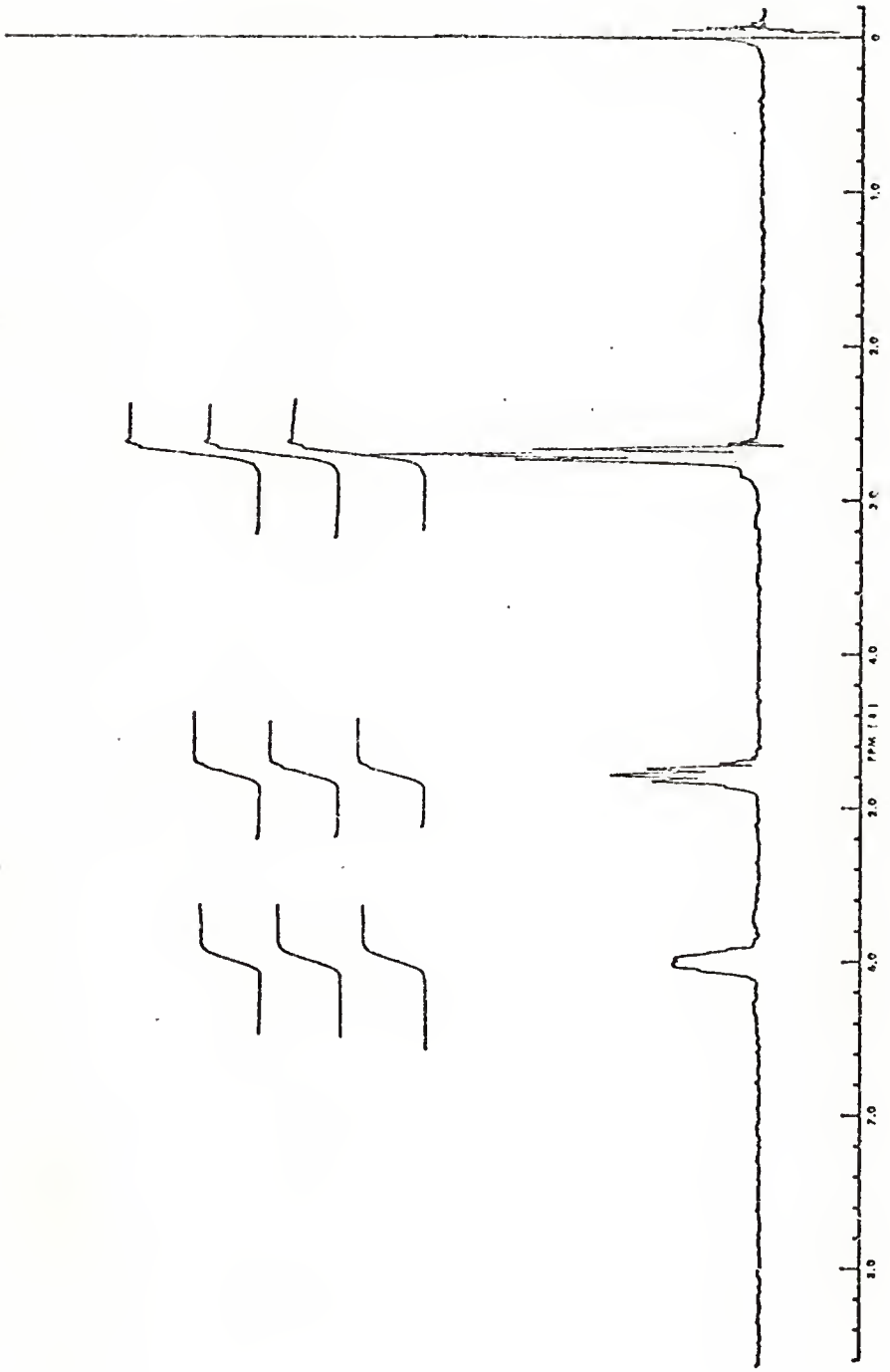


Figure 15: Nmr of 3-methylene-1,1-di(vinyl-2,2-d_2)cyclobutane (2-d_4)

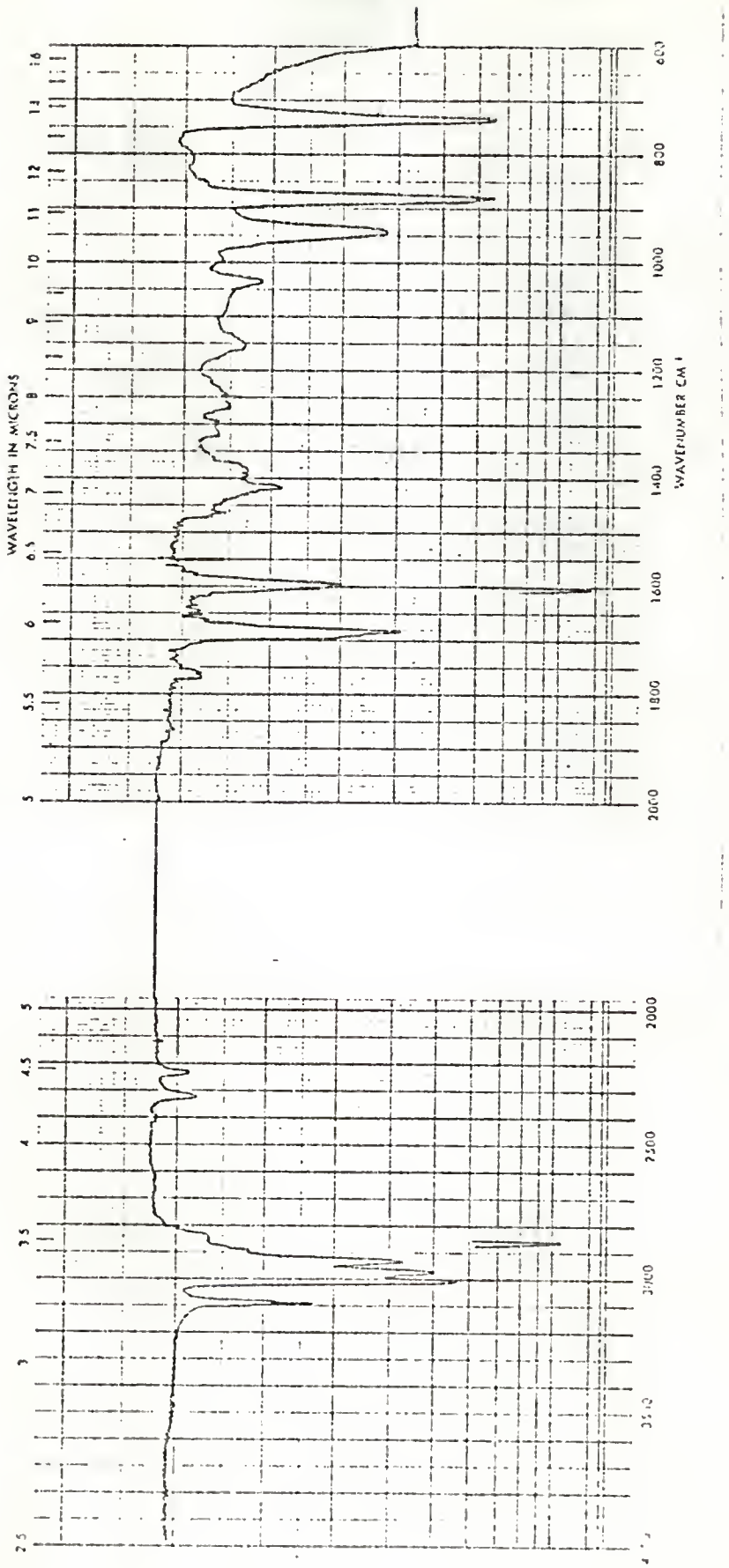


Figure 16: Ir of 3-methylene-1,1-di(vinyl-2,2-$\underline{d}_2$)cyclobutane (2-$\underline{d}_4$)

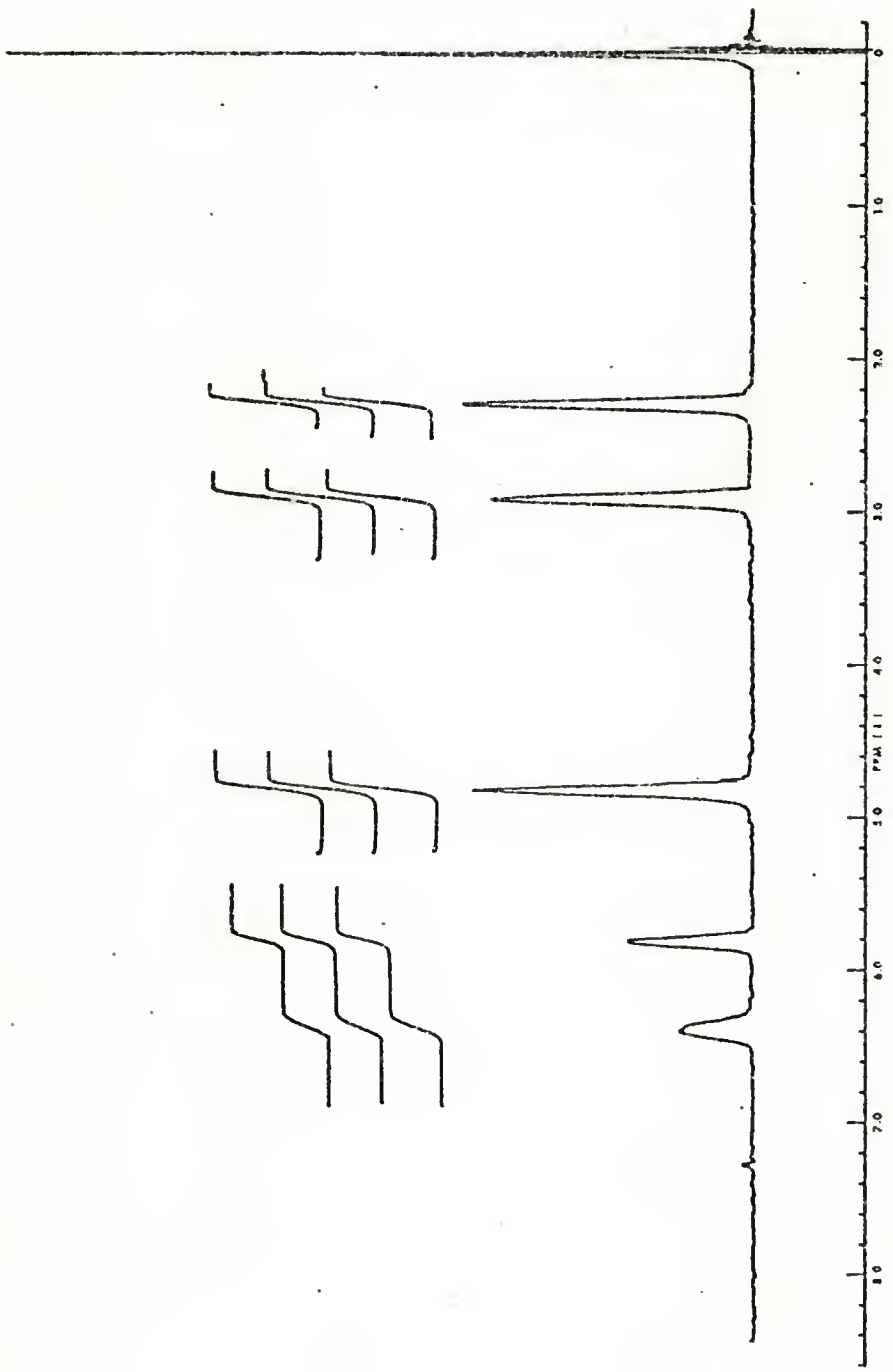


Figure 17: Nmr of 4-methylene-2-(vinyl-2,2-$\underline{d}_2$)cyclohexene-$\underline{6}$,$\underline{6}$-$\underline{d}_2$ (3-$\underline{d}_4$)

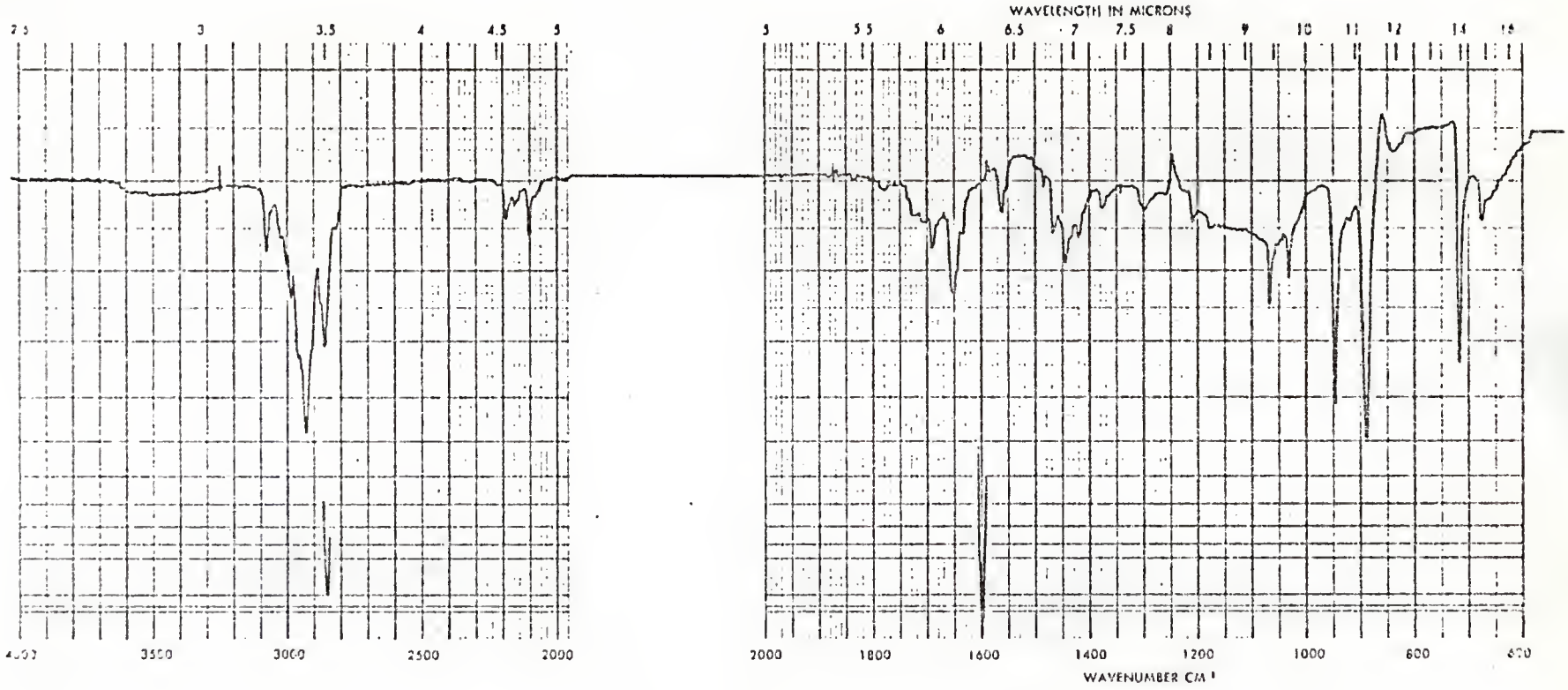


Figure 18: Ir of 4-methylene-2-(vinyl-$\underline{2}$,$\underline{2}$-$\underline{d}_2$)cyclohexene-$\underline{6}$,$\underline{6}$-$\underline{d}_2$ ($\underline{3}$-$\underline{d}_4$)

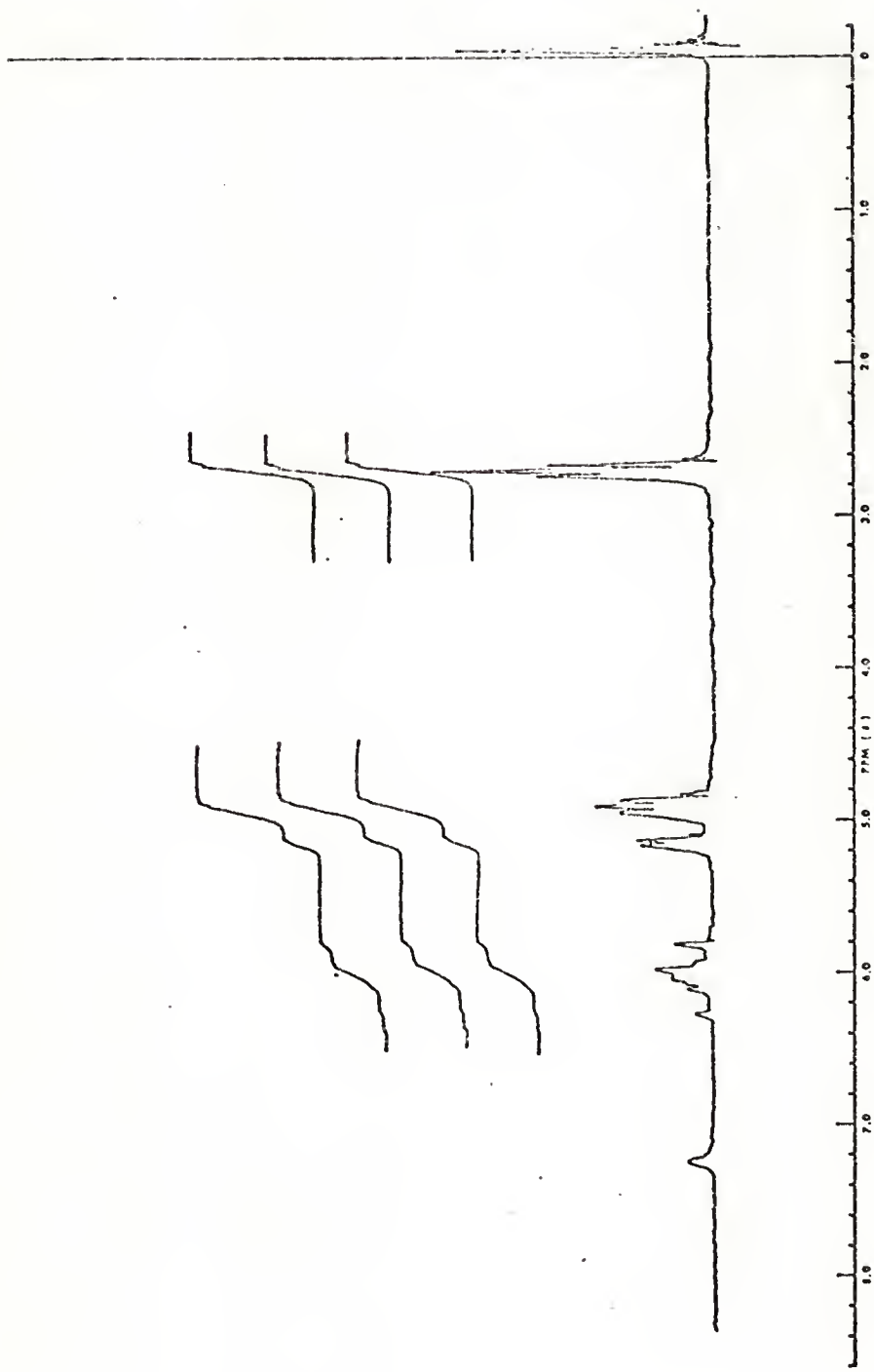


Figure 19: Nmr of 3-methylene-1-vinyl-1-(vinyl-$\underline{2}$,2-$\underline{d}_2$)cyclobutane (2-$\underline{d}_2$)

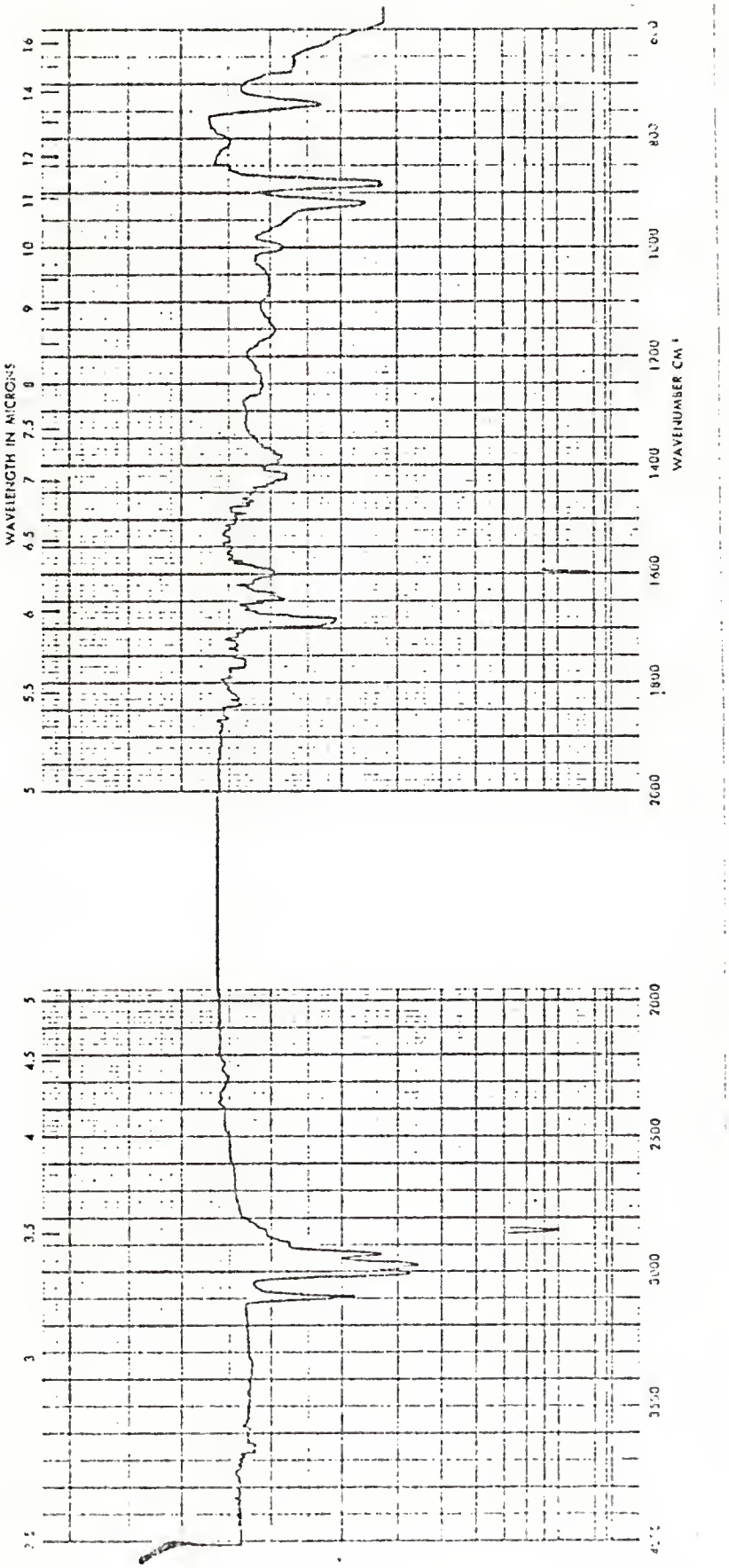


Figure 20: Ir of 3-methylene-1-vinyl-1-(vinyl-2,2-$\underline{d}_2$)cyclobutane (2-$\underline{d}_2$)

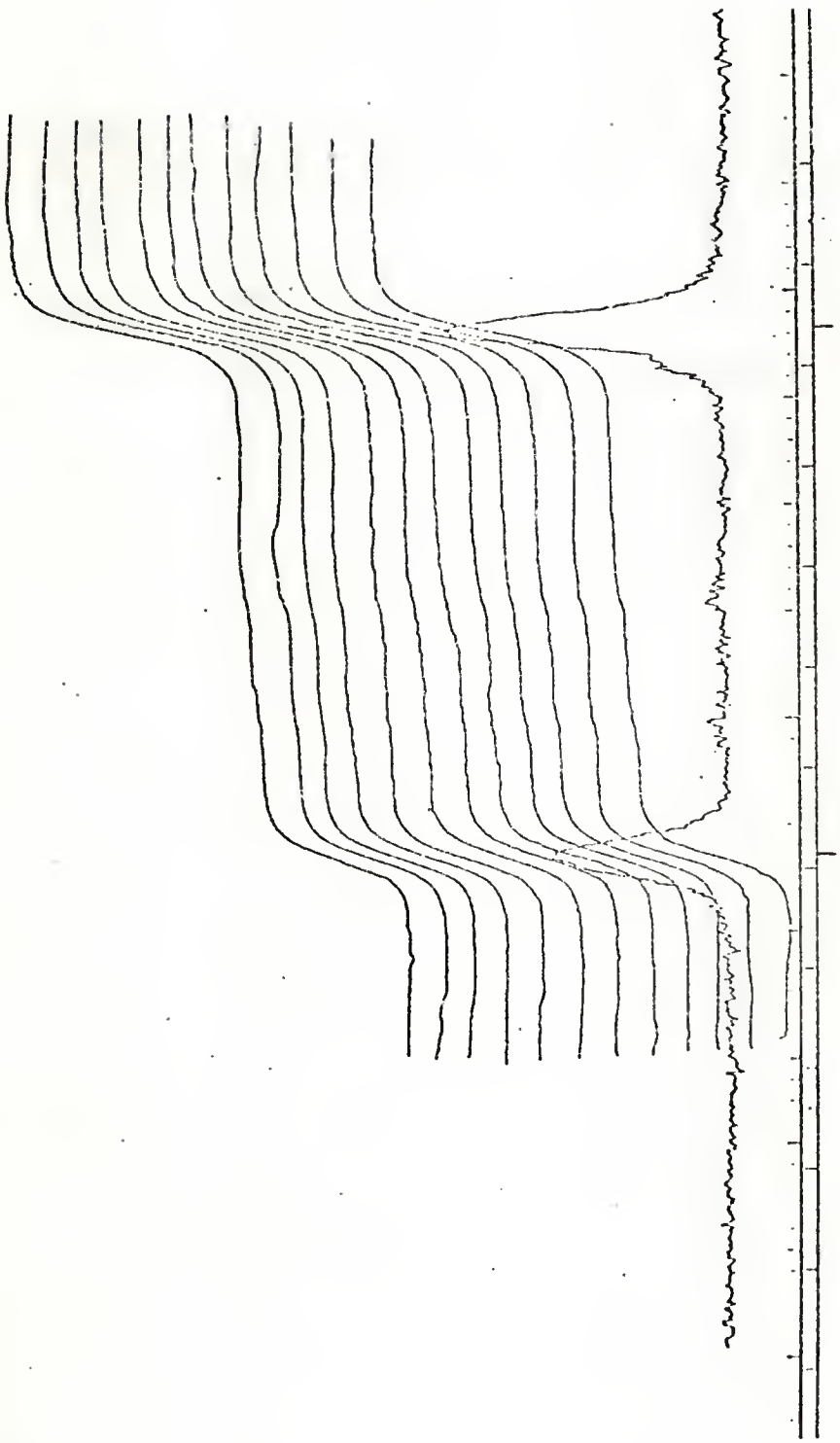


Figure 21: Aliphatic region of the nmr (100 MHz) for the mixture of dideuterated 4-methylene-2-vinylcyclohexenes (3a) and (3b)

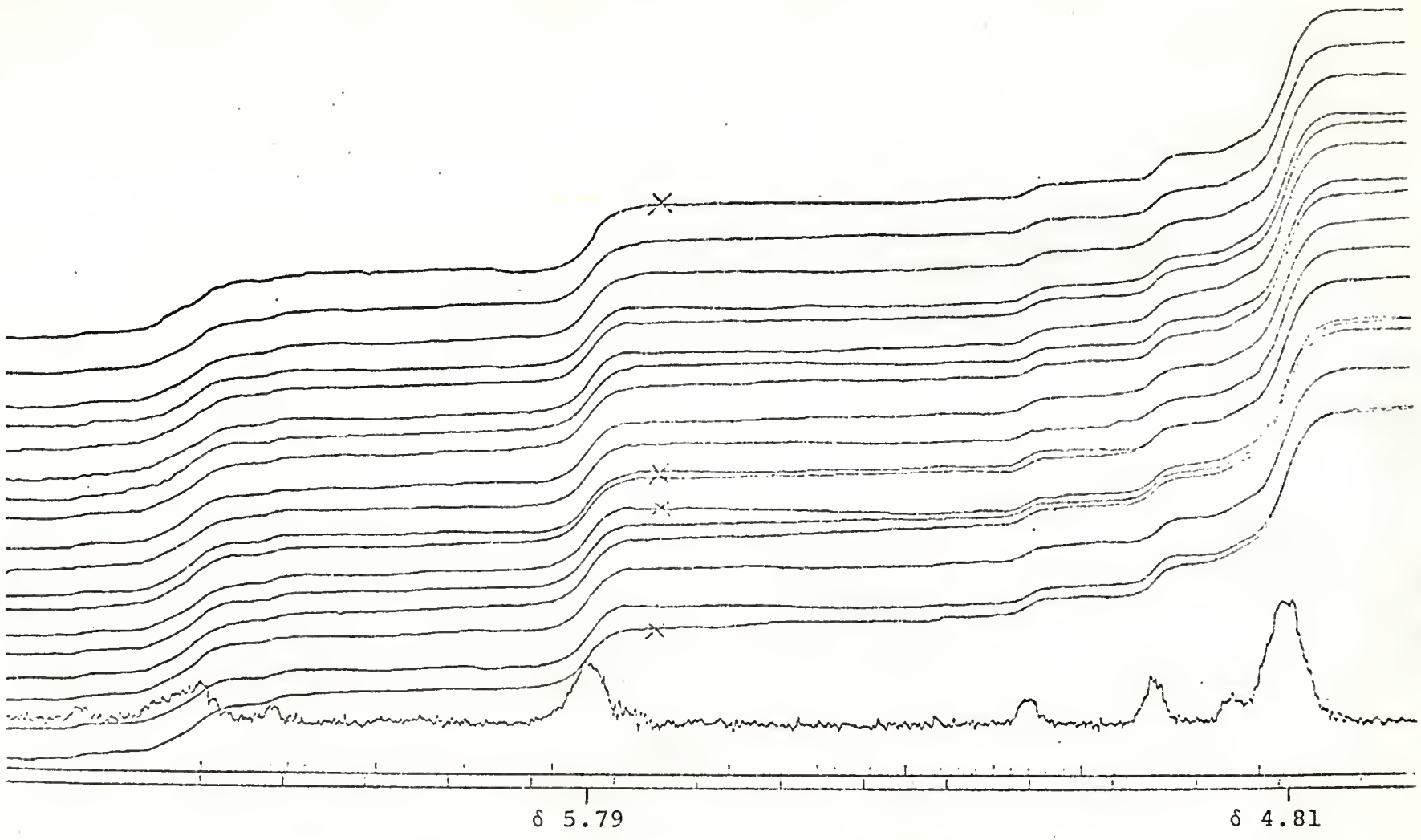


Figure 22: Vinylic region of the nmr (100 MHz) for the mixture of dideuterated 4-methylene-2-vinylcyclohexenes (3a) and (3b)

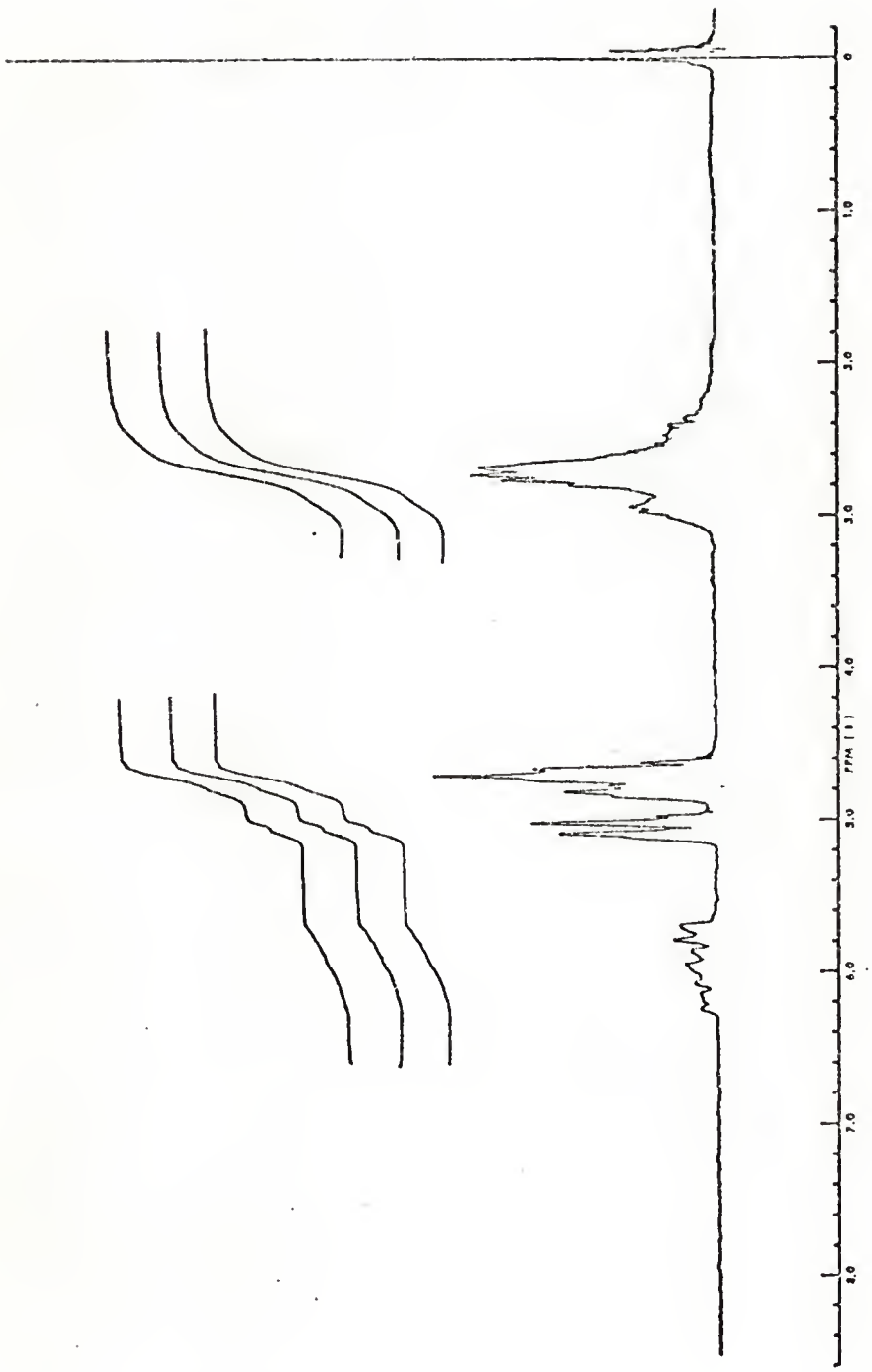


Figure 23: Nmr of methylene-3-vinylcyclobutane (29)

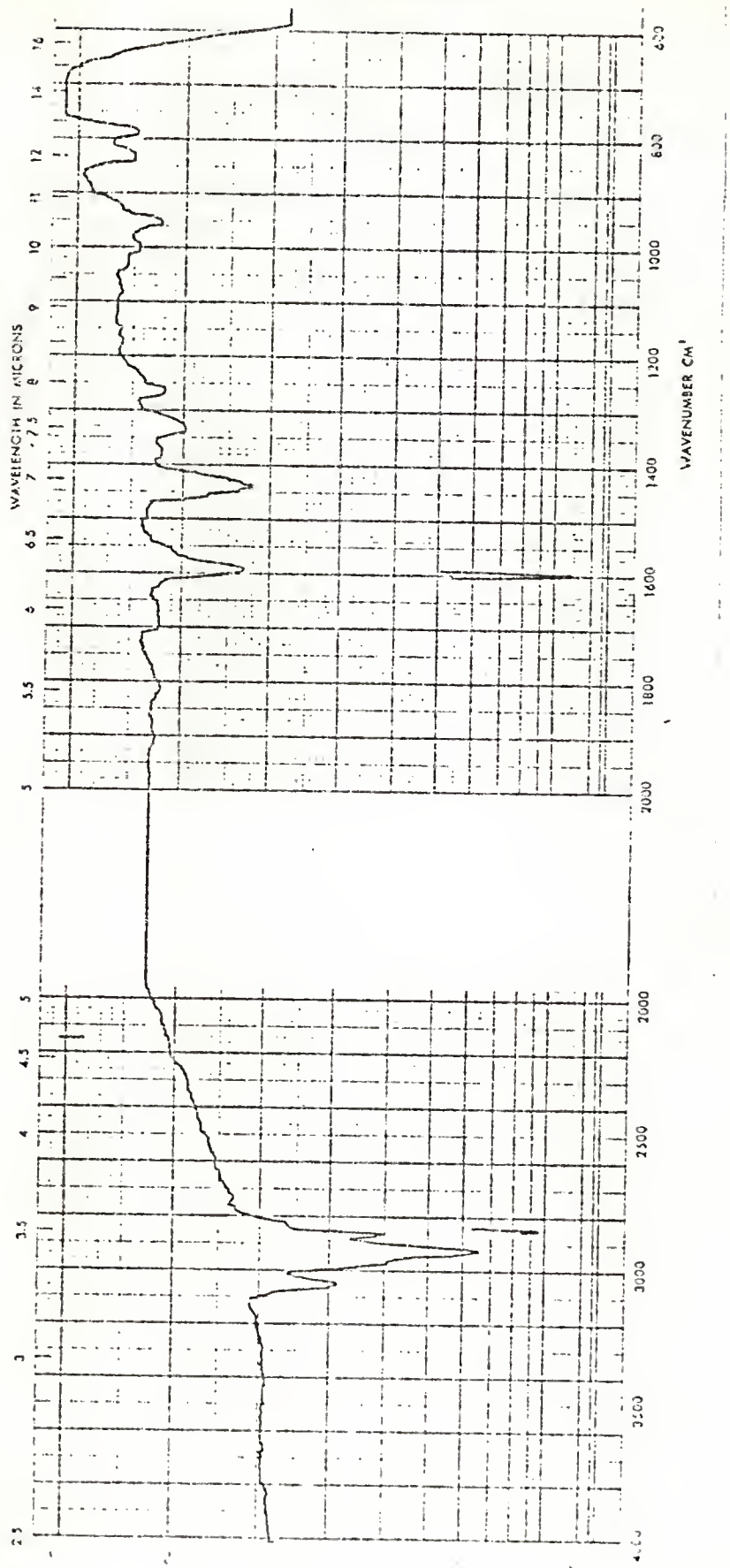


Figure 24: Ir of methylene-3-vinylcyclobutane (29)

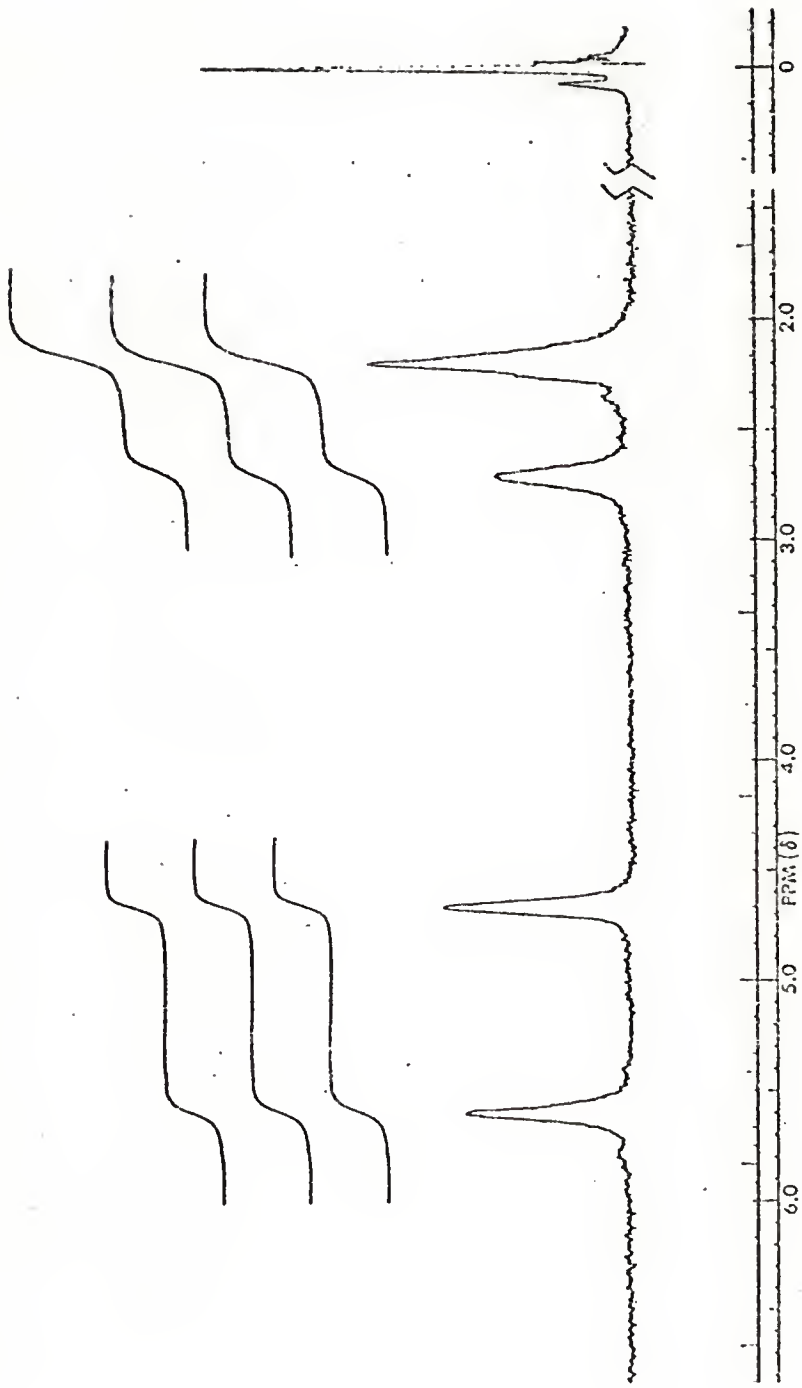


Figure 25: Nmr of 4-methylenecyclohexene (30)

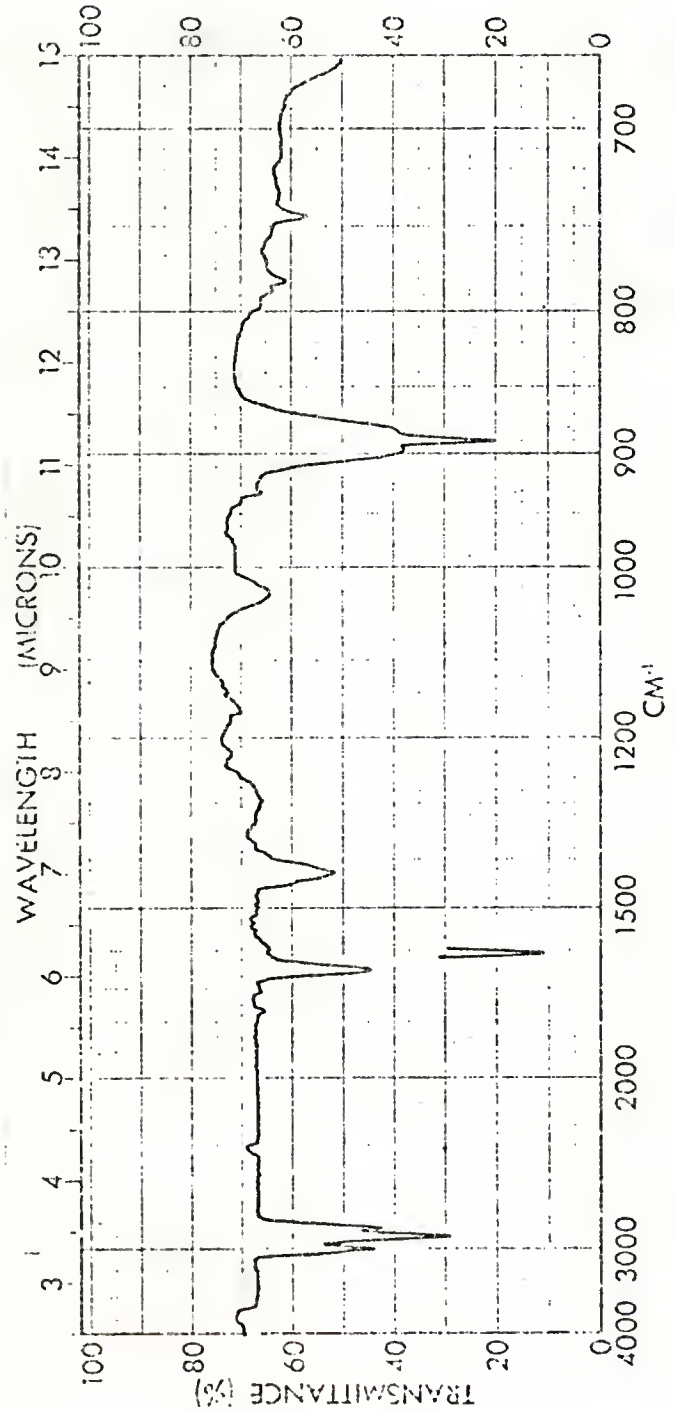


Figure 26: Ir of 4-methylenecyclohexene (30)

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Gregory J. Mancini was born on March 19, 1946 in Irvington, New Jersey. He attended public and parochial schools and South Brunswick High School. He graduated cum laude from Rutgers, The State University, New Brunswick, New Jersey, in 1968 as a member of Phi Beta Kappa and with a bachelor's degree in chemistry. He attended the University of Florida until 1975, graduating with a Ph. D. in organic chemistry. He is single and now free!

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

William R. Dolbier, Jr., Chairman
Associate Professor of Chemistry

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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